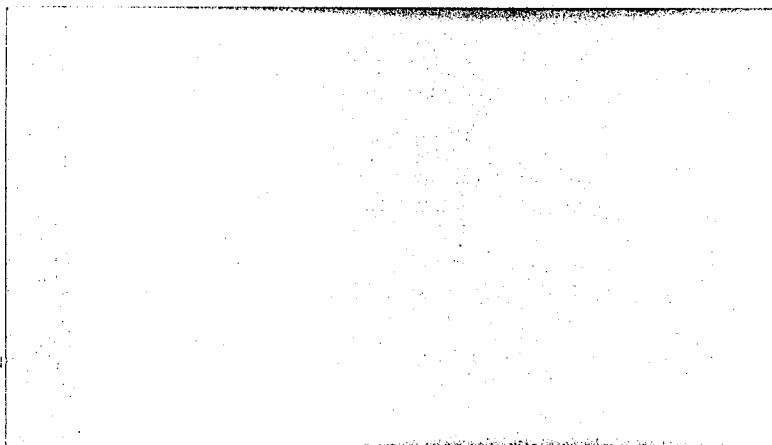


LITIGATION TECHNICAL SUPPORT AND SERVICES

ROCKY MOUNTAIN ARSENAL

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VOLUME IV
ORIGINAL



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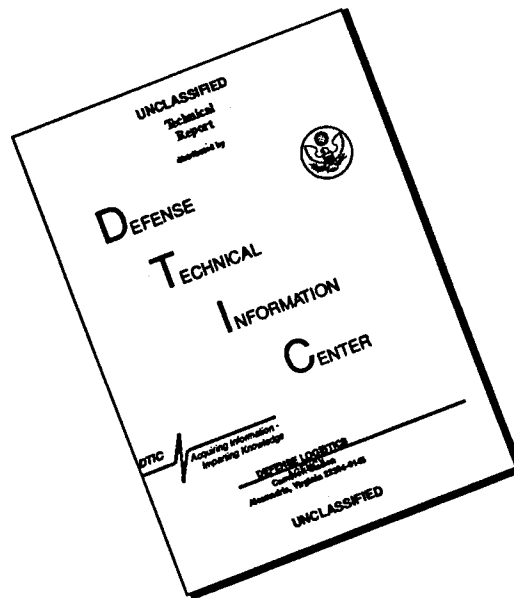
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EBASCO SERVICES INCORPORATED

PROJECT SPECIFIC ANALYTICAL METHODS MANUAL
FOR
AN ENVIRONMENTAL PROGRAM IN SUPPORT OF
LITIGATION AT ROCKY MOUNTAIN ARSENAL

APPROVED BY:

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SECTION A

VOLATILE COMPOUNDS IN AIR USING ACTIVATED CHARCOAL AND TENAX
SAMPLING TUBES

UBTL METHOD DEVELOPED FOR NIOSH

PROPOSED METHOD

Identification of Volatile Compounds in Air using Activated Charcoal and Tenax Sampling Tubes.

I. Application: This method is designed for use as a reconnaissance screening tool. The charcoal is desorbed with dichloromethane; and the Tenax is desorbed with isooctane. The extracts are analyzed by capillary column GC/MS in order to identify unknown compounds. This method is not certified.

- A. Proposed Concentration Range: N/A
- B. Sensitivity: Response should be ten times background noise or better for the selected ions.
- C. Proposed detection limit: N/A
- D. Interferences: Coeluting compounds with similar ions could interfere with identification.
- E. Analysis Rate: One analyst can analyze eight samples in an eight hour day.

II. Chemistry

- A. Nomenclature: N/A
- B. Physical and Chemical Properties: N/A
- C. Chemical Reactions: N/A

III. Apparatus

- A. Instrumentation: Dupont Model DP-1. GC/MS equipped with a fused silica capillary column.
- B. Parameters: Typical parameters are listed below. They may be modified to accomodate samples from different locations.
 - 1. Column: 30m DB-5 fused silica programmed from 40°C to 270°C.
 - 2. GC Conditions: Injector port 290°C; source: 200°C; helium carrier gas.

3. Injection volume: 20L
4. Retention time: N/A

C. Hardware/Glassware:

1. Dichloromethane and isooctane, Burdick and Jackson pesticide grade (or equivalent).

IV. Standards: N/A

V. Procedure

The charcoal and Tenax are desorbed for 1 hour with occasional shaking in dichloromethane and isooctane, respectively. The instrument is tuned to DF TPP.

Sufficiently intense unknown peaks (approximately ten per sample are anticipated) will be tentatively identified by computer assisted comparison to the NBS mass spectral library. The report will contain a calculated value which reflects the reliability of the possible matches. The mass spectroscopists judgement of high, moderate or low probability of correct assignment will also be included. Hard copy mass spectra of all unknowns will be provided with the report.

SECTION B

INTERIM METHOD FOR THE DETERMINATION OF ASBESTOS
IN BULK ISOLATION SAMPLES

EPA-600-M4-82-020, DECEMBER 1982



Test Method

Interim Method for the Determination of Asbestos in Bulk Insulation Samples*

1. Polarized Light Microscopy

1.1 Principle and Applicability

Bulk samples of building materials taken for asbestos identification are first examined for homogeneity and preliminary fiber identification at low magnification. Positive identification of suspect fibers is made by analysis of subsamples with the polarized light microscope.

The principles of optical mineralogy are well established.^{1,2} A light microscope equipped with two polarizing filters is used to observe specific optical characteristics of a sample. The use of plane polarized light allows the determination of refractive indices along specific crystallographic axes. Morphology and color are also observed. A retardation plate is placed in the polarized light path for determination of the sign of elongation using orthoscopic illumination. Orientation of the two filters such that their vibration planes are perpendicular (crossed polars) allows observation of the birefringence and extinction characteristics of anisotropic particles.

Quantitative analysis involves the use of point counting. Point counting is a standard technique in petrography for determining the relative areas occupied by separate minerals in thin sections of rock. Background information on the use of point counting³ and the interpretation of point count data³ is available.

*An interim method is carefully drafted from available source information. This method is still under investigation and therefore is subject to revision.

This method is applicable to all bulk samples of friable insulation materials submitted for identification and quantitation of asbestos components.

1.2 Range

The point counting method may be used for analysis of samples containing from 0 to 100 percent asbestos. The upper detection limit is 100 percent. The lower detection limit is less than 1 percent.

1.3 Interferences

Fibrous organic and inorganic constituents of bulk samples may interfere with the identification and quantitation of the asbestos mineral content. Spray-on binder materials may coat fibers and affect color or obscure optical characteristics to the extent of masking fiber identity. Fine particles of other materials may also adhere to fibers to an extent sufficient to cause confusion in identification. Procedures that may be used for the removal of interferences are presented in Section 1.7.2.2.

1.4 Precision and Accuracy

Adequate data for measuring the accuracy and precision of the method for samples with various matrices are not currently available. Data obtained for samples containing a single asbestos type in a simple matrix are available in the EPA report *Bulk Sample Analysis for Asbestos Content: Evaluation of the Tentative Method*.⁴

1.5 Apparatus

1.5.1 Sample Analysis

A low-power binocular microscope, preferably stereoscopic, is used to

examine the bulk insulation sample as received.

- **Microscope:** binocular, 10-45X (approximate)
- **Light Source:** incandescent or fluorescent
- **Forceps, Dissecting Needles, and Probes**
- **Glassine Paper or Clean Glass Plate**

Compound microscope requirements: A polarized light microscope complete with polarizer, analyzer, port for wave retardation plate, 360° graduated rotating stage, substage condenser, lamp, and lamp iris.

- **Polarized Light Microscope:** described above
- **Objective Lenses:** 10X, 20X, and 40X or near equivalent
- **Dispersion Staining Objective Lens** (optional)
- **Ocular Lens:** 10X minimum
- **Eyeiece Reticle:** cross hair or 25 point Chalkley Point Array
- **Compensator Plate:** 550 milli-micron retardation

1.5.2 Sample Preparation

Sample preparation apparatus requirements will depend upon the type of insulation sample under consideration. Various physical and/or chemical means may be employed for an adequate sample assessment.

- **Ventilated Hood** or negative pressure glove box
- **Microscope Slides**
- **Coverslips**
- **Mortar and Pestle:** agate or porcelain (optional)
- **Wylie Mill** (optional)
- **Beakers & assorted glassware** (optional)
- **Centrifuge** (optional)
- **Filtration apparatus** (optional)
- **Low temperature asher** (optional)

1.6 Reagents

1.6.1 Sample Preparation

- **Distilled Water** (optional)
- **Dilute CH_3COOH :** ACS reagent grade (optional)
- **Dilute HCl :** ACS reagent grade (optional)
- **Sodium metaphosphate (NaPO_3):** (optional)

1.6.2 Analytical Reagents

- **Refractive Index Liquids:** 1.490-1.570, 1.590-1.720 in increments of 0.002 or 0.004
- **Refractive Index Liquids for Dispersion Staining:** high-dispersion series, 1.550, 1.605, 1.630 (optional)
- **UICC Asbestos Reference Sample Set:** Available from: UICC MRC

Pneumoconiosis Unit, Llandough Hospital, Penarth, Glamorgan CF6 1XW, UK, and commercial distributors

- **Tremolite-asbestos** (source to be determined)
- **Actinolite-asbestos** (source to be determined)

1.7 Procedures

Note: Exposure to airborne asbestos fibers is a health hazard. Bulk samples submitted for analysis are usually friable and may release fibers during handling or matrix reduction steps. All sample and slide preparations should be carried out in a ventilated hood or glove box with continuous airflow (negative pressure). Handling of samples without these precautions may result in exposure of the analyst and contamination of samples by airborne fibers.

1.7.1 Sampling

Samples for analysis of asbestos content shall be taken in the manner prescribed in Reference 5 and information on design of sampling and analysis programs may be found in Reference 6. If there are any questions about the representative nature of the sample, another sample should be requested before proceeding with the analysis.

1.7.2 Analysis

1.7.2.1 Gross Examination

Bulk samples of building materials taken for the identification and quantitation of asbestos are first examined for homogeneity at low magnification with the aid of a stereomicroscope. The core sample may be examined in its container or carefully removed from the container onto a glassine transfer paper or clean glass plate. If possible, note is made of the orientation of top and bottom surfaces. When discrete strata are identified, each is treated as a separate material so that fibers are first identified and quantified in that layer only, and then the results for each layer are combined to yield an estimate of asbestos content for the whole sample.

1.7.2.2 Sample Preparation

Bulk materials submitted for asbestos analysis involve a wide variety of matrix materials. Representative subsamples may not be readily obtainable by simple means in heterogeneous materials, and various steps may be required to alleviate the difficulties encountered. In most cases, however, the best preparation is made by using forceps to sample at several places from the bulk material. Forcep samples are immersed in a refractive index liquid on a microscope slide,

teased apart, covered with a cover glass, and observed with the polarized light microscope.

Alternatively, attempts may be made to homogenize the sample or eliminate interferences before further characterization. The selection of appropriate procedures is dependent upon the samples encountered and personal preference. The following are presented as possible sample preparation steps.

A mortar and pestle can sometimes be used in the size reduction of soft or loosely bound materials, though this may cause matting of some samples. Such samples may be reduced in a Wiley mill. Apparatus should be clean and extreme care exercised to avoid cross-contamination of samples. Periodic checks of the particle sizes should be made during the grinding operation so as to preserve any fiber bundles present in an identifiable form. These procedures are not recommended for samples that contain amphibole minerals or vermiculite. Grinding of amphiboles may result in the separation of fiber bundles or the production of cleavage fragments that have aspect ratios greater than 3:1 and will be classified as asbestos fibers. Grinding of vermiculite may also produce fragments with aspect ratios greater than 3:1.

Acid treatment may occasionally be required to eliminate interferences. Calcium carbonate, gypsum, and bassanite (plaster) are frequently present in sprayed or trowelled insulations. These materials may be removed by treatment with warm dilute acetic acid. Warm dilute hydrochloric acid may also be used to remove the above materials. If acid treatment is required, wash the sample at least twice with distilled water, being careful not to lose the particulates during decanting steps. Centrifugation or filtration of the suspension will prevent significant fiber loss. The pore size of the filter should be 0.45 micron or less.

Caution: prolonged acid contact with the sample may alter the optical characteristics of chrysotile fibers and should be avoided.

Coatings and binding materials adhering to fiber surfaces may also be removed by treatment with sodium metaphosphate.⁷ Add 10 mL of 10 g/L sodium metaphosphate solution to a small (0.1 to 0.5 mL) sample of bulk material in a 15-mL glass centrifuge tube. For approximately 15 seconds each, stir the mixture on a vortex mixer, place in an ultrasonic bath and then shake by hand. Repeat the series.

Collect the dispersed solids by centrifugation at 1000 rpm for 5 minutes. Wash the sample three times by suspending in 10 mL distilled water and recentrifuging. After washing, resuspend the pellet in 5 mL distilled water, place a drop of the suspension on a microscope slide, and dry the slide at 110°C.

In samples with a large portion of cellulosic or other organic fibers, it may be useful to ash part of the sample and examine the residue. Ashing should be performed in a low temperature ashers. Ashing may also be performed in a muffle furnace at temperatures of 500°C or lower. Temperatures of 550°C or higher will cause dehydroxylation of the asbestos minerals, resulting in changes of the refractive index and other key parameters. If a muffle furnace is to be used, the furnace thermostat should be checked and calibrated to ensure that samples will not be heated at temperatures greater than 500°C.

Ashing and acid treatment of samples should not be used as standard procedures. In order to monitor possible changes in fiber characteristics, the material should be viewed microscopically before and after any sample preparation procedure. Use of these procedures on samples to be used for quantitation requires a correction for percent weight loss.

1.7.2.3 Fiber Identification

Positive identification of asbestos requires the determination of the following optical properties.

- Morphology
- Color and pleochroism
- Refractive indices
- Birefringence
- Extinction characteristics
- Sign of elongation

Table 1-1 lists the above properties for commercial asbestos fibers. Figure 1-1 presents a flow diagram of the examination procedure. Natural variations in the conditions under which deposits of asbestiform minerals are formed will produce exceptions to the published values and differences from the UICC standards. The sign of elongation is determined by use of the compensator plate and crossed polars. Refractive indices may be determined by the Becke line test. Alternatively, dispersion staining may be used. Inexperienced operators may find that the dispersion staining technique is more easily learned, and should consult Reference 9 for guidance. Central stop dispersion staining colors are presented in Table

1-2 Available high dispersion (HD) liquids should be used

1.7.2.4 Quantitation of Asbestos Content

Asbestos quantitation is performed by a point-counting procedure. An ocular reticle (cross-hair or point array) is used to visually superimpose a point or points on the microscope field of view. Record the number of points positioned directly above each kind of particle or fiber of interest. Score only points directly over asbestos fibers or nonasbestos matrix material. Do not score empty points for the closest particle. If an asbestos fiber and a matrix particle overlap so that a point is superimposed on their visual intersection, a point is scored for both categories. Point counting provides a determination of the area percent asbestos. Reliable conversion of area percent to percent of dry weight is not currently feasible unless the specific gravities and relative volumes of the materials are known.

For the purpose of this method, "asbestos fibers" are defined as having an aspect ratio greater than 3:1 and being positively identified as one of the minerals in Table 1-1.

A total of 400 points superimposed on either asbestos fibers or nonasbestos matrix material must be counted over at least eight different preparations of representative subsamples. Take eight forcep samples and mount each separately with the appropriate refractive index liquid. The preparation should not be heavily loaded. The sample should be uniformly dispersed to avoid overlapping particles and allow 25-50 percent empty area within the fields of view. Count 50 nonempty points on each preparation, using either

- A cross-hair reticle and mechanical stage; or
- A reticle with 25 points (Chalkley Point Array) and counting at least 2 randomly selected fields.

For samples with mixtures of isotropic and anisotropic materials present, viewing the sample with slightly uncrossed polars or the addition of the compensator plate to the plane polarized light path will allow simultaneous discrimination of both particle types. Quantitation should be performed at 100X or at the lowest magnification of the polarized light microscope that can effectively distinguish the sample components. Confirmation of the quantitation result by a second analyst on some percentage of analyzed samples should be used as standard quality control procedure.

The percent asbestos is calculated as follows

$$\% \text{ asbestos} = (a/n) 100\%$$

where

a = number of asbestos counts,
n = number of nonempty points counted (400).

If a = 0, report "No asbestos detected." If $0 < a \leq 3$, report "<1% asbestos."

The value reported should be rounded to the nearest percent.

1.8 References

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8. W. J. Campbell, R. L. Blake, L. L. Brown, E. E. Cather, and J. J. Sjöberg, *Selected Silicate Minerals and Their Asbestiform Varieties: Mineralogical Definitions and Identification-Characterization*, U.S. Bureau of Mines Information Circular 8751, 1977.
9. Walter C. McCrone, *Asbestos Particle Atlas*, Ann Arbor: Ann Arbor Science Publishers, June 1980.

Table 1-1. Optical properties of asbestos fibers

Mineral	Morphology, color ¹	Refractive indices ²		Birefringence	Extinction	Sign of elongation
		α	γ			
Chrysotile (asbestiform serpentine)	Wavy fibers. Fiber bundles have splayed ends and "kinks". Aspect ratio typically >10:1. Colorless ³ , nonpleochroic.	1.493-1.560	1.517-1.562 ⁴ (normally 1.556)	.002-.014	to fiber length	+ (length slow)
Amosite (asbestiform grunerite)	Straight, rigid fibers. Aspect ratio typically >10:1. Colorless to brown, nonpleochroic or weakly so. Opaque inclusions may be present.	1.635-1.696	1.655-1.729 ⁵ (normally 1.696-1.710)	.020-.033	to fiber length	+ (length slow)
Crocidolite (asbestiform riebeckite)	Straight, rigid fibers. Thick fibers and bundles common, blue to purple-blue in color. Pleochroic. Birefringence is generally masked by blue color.	1.654-1.701	1.668-1.717 ⁵ (normally close to 1.700)	.014-.016	to fiber length	— (length fast)
Anthophyllite- asbestos	Straight, single fibers, some larger composite fibers. Anthophyllite cleavage fragments may be present with aspect ratios <10:1. ⁴ Colorless to light brown.	1.596-1.652	1.615-1.676 ⁵	.019-.024	to fiber length	+ (length slow)
Tremolite- actinolite- asbestos	Tremolite-asbestos may be present as single or composite fibers. Tremolite cleavage fragments may be present as single crystals with aspect ratios <10:1. ⁴ Colorless to pale green.	1.599-1.668	1.622-1.688 ⁶	.023-.020	Oblique extinction, 10-20° for fragments. Composite fibers show extinction.	+ (length slow)

¹ From reference 5, colors cited are seen by observation with plane polarized light

² From references 5 and 8.

³ Fibers subjected to heating may be brownish.

⁴ Fibers defined as having aspect ratio >3:1.

⁵ \perp to fiber length.

⁶ || to fiber length.

Table 1-2. Central stop dispersion staining colors^a

Mineral	RI Liquid	\perp	
Chrysotile	1.550 ^{MD}	Blue	Blue-magenta
"Amosite"	1.680	Blue-magenta to pale blue	Golden-yellow
	1.550 ^{MD}	Yellow to white	Yellow to white
Crocidolite ^b	1.700	Red magenta	Blue-magenta
	1.550 ^{MD}	Yellow to white	Yellow to white
Anthophyllite- asbestos	1.605 ^{MD}	Blue	Gold to gold-magenta
Tremolite- asbestos	1.605 ^{MDc}	Pale blue	Yellow
Actinolite- asbestos	1.605 ^{MD}	Gold-magenta to blue	Gold
	1.630 ^{MDc}	Magenta	Golden-yellow

^a From reference 9, colors may vary slightly.

^b Blue absorption color.

^c Oblique extinction view.

Polarized light microscopy qualitative analysis: For each type of material identified by examination of sample at low magnification. Mount spacially dispersed sample in 1.550 RI liquid (If using dispersion staining, mount in 1.550 HD.) View at 100X with both plane polarized light and crossed polars. More than one fiber type may be present.

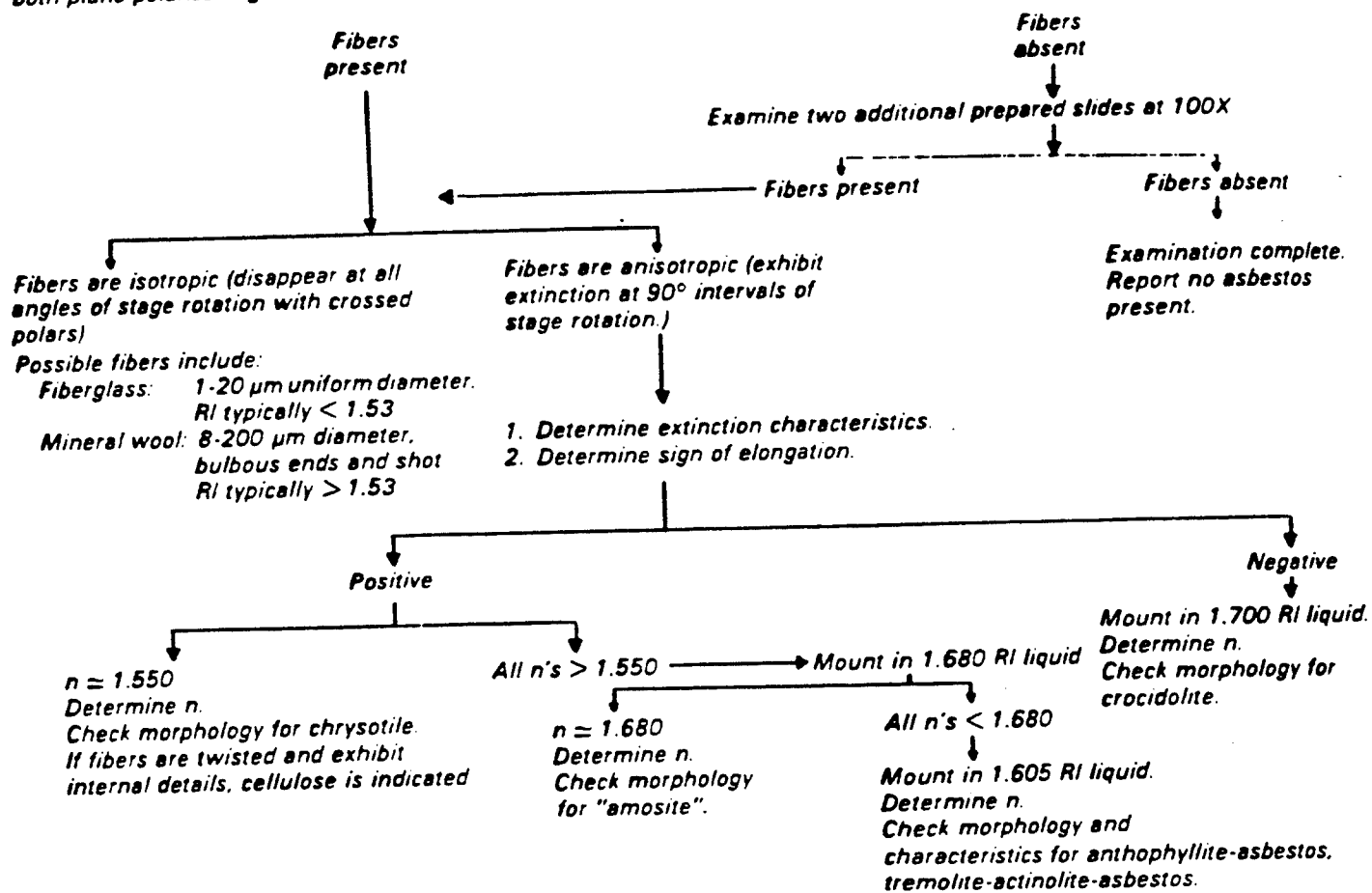


Figure 1-1. Flow chart for qualitative analysis of bulk samples by polarized light microscopy.

2. X-Ray Powder Diffraction

2.1 Principle and Applicability

The principle of X-ray powder diffraction (XRD) analysis is well established.^{1,2} Any solid, crystalline material will diffract an impinging beam of parallel, monochromatic X-rays whenever Bragg's Law,

$$\lambda = 2d \sin \theta,$$

is satisfied for a particular set of planes in the crystal lattice, where

λ = the X-ray wavelength, Å;

d = the interplanar spacings of the set of reflecting lattice planes, Å; and

θ = the angle of incidence between the X-ray beam and the reflecting lattice planes.

By appropriate orientation of a sample relative to the incident X-ray beam, a diffraction pattern can be generated that, in most cases, will be uniquely characteristic of both the chemical composition and structure of the crystalline phases present.

Unlike optical methods of analysis, however, XRD cannot determine crystal morphology. Therefore, in asbestos analysis, XRD does not distinguish between fibrous and nonfibrous forms of the serpentine and amphibole minerals (Table 2-1). However, when used in conjunction with optical methods such as polarized light microscopy (PLM), XRD techniques can provide a reliable analytical method for the identification and characterization of asbestiform minerals in bulk materials.

For *qualitative analysis* by XRD methods, samples are initially scanned over limited diagnostic peak regions for the serpentine (~7.4 Å) and amphibole (8.2-8.5 Å) minerals (Table 2-2). Standard slow-scanning methods for bulk sample analysis may be used for materials shown by PLM to contain significant amounts of asbestos (>5-10 percent). Detection of minor or trace amounts of asbestos may require special sample preparation and step-scanning analysis. All samples that exhibit diffraction peaks in the diagnostic regions for asbestiform minerals are submitted to a full (5°-60° 2 θ ; 1° 2 θ /min) qualitative XRD scan, and their diffraction patterns are compared with standard reference powder diffraction patterns³ to verify initial peak assignments and to identify possible matrix interferences when

subsequent quantitative analysis will be performed.

Accurate *quantitative analysis* of asbestos in bulk samples by XRD is critically dependent on particle size distribution, crystallite size, preferred orientation and matrix absorption effects, and comparability of standard reference and sample materials. The most intense diffraction peak that has been shown to be free from interference by prior qualitative XRD analysis is selected for quantitation of each asbestiform mineral. A "thin-layer" method of analysis^{8,9} is recommended in which, subsequent to comminution of the bulk material to ~10 μ m by suitable cryogenic milling techniques, an accurately known amount of the sample is deposited on a silver membrane filter. The mass of asbestiform material is determined by measuring the integrated area of the selected diffraction peak using a step-scanning mode, correcting for matrix absorption effects, and comparing with suitable calibration standards. Alternative "thick-layer" or bulk methods^{7,8} may be used for *semiquantitative analysis*.

This XRD method is applicable as a confirmatory method for identification and quantitation of asbestos in bulk material samples that have undergone prior analysis by PLM or other optical methods.

2.2 Range and Sensitivity

The range of the method has not been determined.

The sensitivity of the method has not been determined. It will be variable and dependent upon many factors, including matrix effects (absorption and interferences), diagnostic reflections selected, and their relative intensities.

2.3 Limitations

2.3.1 Interferences

Since the fibrous and nonfibrous forms of the serpentine and amphibole minerals (Table 2-1) are indistinguishable by XRD techniques unless special sample preparation techniques and instrumentation are used,⁹ the presence of nonasbestiform serpentines and amphiboles in a sample will pose severe interference problems in the identification and quantitative analysis of their asbestiform analogs.

The use of XRD for identification and quantitation of asbestiform minerals in bulk samples may also be limited by the presence of other interfering materials in the sample. For naturally occurring materials the commonly associated asbestos-related mineral interferences can usually be anticipated. However, for fabricated materials the nature of the interferences may vary greatly (Table 2-3) and present more serious problems in identification and quantitation.¹⁰ Potential interferences are summarized in Table 2-4 and include the following:

- *Chlorite* has major peaks at 7.19 Å and 3.58 Å that interfere with both the primary (7.36 Å) and secondary (3.66 Å) peaks for chrysotile. Resolution of the primary peak to give good quantitative results may be possible when a step-scanning mode of operation is employed.
- *Halloysite* has a peak at 3.63 Å that interferes with the secondary (3.66 Å) peak for chrysotile.
- *Keolinite* has a major peak at 7.15 Å that may interfere with the primary peak of chrysotile at 7.36 Å when present at concentrations of >10 percent. However, the secondary chrysotile peak at 3.66 Å may be used for quantitation.
- *Gypsum* has a major peak at 7.5 Å that overlaps the 7.36 Å peak of chrysotile when present as a major sample constituent. This may be removed by careful washing with distilled water, or by heating to 300°C to convert gypsum to plaster of paris.
- *Cellulose* has a broad peak that partially overlaps the secondary (3.66 Å) chrysotile peak.⁸
- Overlap of major diagnostic peaks of the amphibole asbestos minerals, amosite, anthophyllite, crocidolite, and tremolite, at approximately 8.3 Å and 3.1 Å causes mutual interference when these minerals occur in the presence of one another. In some instances adequate resolution may be attained by using step-scanning methods and/or by decreasing the collimator slit width at the X-ray port.
- *Carbonates* may also interfere with quantitative analysis of the amphibole asbestos minerals, amosite,

anthophyllite, crocidolite, and tremolite. Calcium carbonate (CaCO_3) has a peak at 3.035 Å that overlaps major amphibole peaks at approximately 3.1 Å when present in concentrations of >5 percent. Removal of carbonates with a dilute acid wash is possible; however, if present, chrysotile may be partially dissolved by this treatment.¹¹

- A major talc peak at 3.12 Å interferes with the primary tremolite peak at this same position and with secondary peaks of crocidolite (3.10 Å), amosite (3.06 Å), and anthophyllite (3.05 Å). In the presence of talc, the major diagnostic peak at approximately 8.3 Å should be used for quantitation of these asbestiform minerals.

The problem of intraspecies and matrix interferences is further aggravated by the variability of the silicate mineral powder diffraction patterns themselves, which often makes definitive identification of the asbestos minerals by comparison with standard reference diffraction patterns difficult. This variability results from alterations in the crystal lattice associated with differences in isomorphous substitution and degree of crystallinity. This is especially true for the amphiboles. These minerals exhibit a wide variety of very similar chemical compositions, with the result being that their diffraction patterns are characterized by having major (110) reflections of the monoclinic amphiboles and (210) reflections of the orthorhombic anthophyllite separated by less than 0.2 Å.¹²

2.3.2 Matrix Effects

If a copper X-ray source is used, the presence of iron at high concentrations in a sample will result in significant X-ray fluorescence, leading to loss of peak intensity with increased background intensity and an overall decrease in sensitivity. This situation may be corrected by use of an X-ray source other than copper; however, this is often accompanied both by loss of intensity and by decreased resolution of closely spaced reflections. Alternatively, use of a diffracted beam monochromator will reduce background fluorescent radiation, enabling weaker diffraction peaks to be detected.

X-ray absorption by the sample matrix will result in overall attenuation of the diffracted beam and may seriously interfere with quantitative analysis. Absorption effects may be

minimized by using sufficiently "thin" samples for analysis.^{8,13,14} However, unless absorption effects are known to be the same for both samples and standards, appropriate corrections should be made by referencing diagnostic peak areas to an internal standard^{7,8} or filter substrate (Ag) peak.^{5,8}

2.3.3 Particle Size Dependence

Because the intensity of diffracted X-radiation is particle-size dependent, it is essential for accurate quantitative analysis that both sample and standard reference materials have similar particle size distributions. The optimum particle size (i.e., fiber length) range for quantitative analysis of asbestos by XRD has been reported to be 1 to 10 µm.¹⁵ Comparability of sample and standard reference material particle size distributions should be verified by optical microscopy (or another suitable method) prior to analysis.

2.3.4 Preferred Orientation Effects

Preferred orientation of asbestiform minerals during sample preparation often poses a serious problem in quantitative analysis by XRD. A number of techniques have been developed for reducing preferred orientation effects in "thick layer" samples.^{7,8,15} For "thin" samples on membrane filters, the preferred orientation effects seem to be both reproducible and favorable to enhancement of the principal diagnostic reflections of asbestos minerals, actually increasing the overall sensitivity of the method.^{12,14} However, further investigation into preferred orientation effects in both thin layer and bulk samples is required.

2.3.5 Lack of Suitably

Characterized Standard Materials

The problem of obtaining and characterizing suitable reference materials for asbestos analysis is clearly recognized. NIOSH has recently directed a major research effort toward the preparation and characterization of analytical reference materials, including asbestos standards;^{16,17} however, these are not available in large quantities for routine analysis.

In addition, the problem of ensuring the comparability of standard reference and sample materials, particularly regarding crystallite size, particle size distribution, and degree of crystallinity, has yet to be adequately addressed. For example, Langer et al.¹⁸ have observed that in insulating matrices, chrysotile tends to break open into bundles more frequently than amphiboles. This results in a line-broadening effect with a resultant

decrease in sensitivity. Unless this effect is the same for both standard and sample materials, the amount of chrysotile in the sample will be underestimated by XRD analysis. To minimize this problem, it is recommended that standardized matrix reduction procedures be used for both sample and standard materials.

2.4 Precision and Accuracy

Precision of the method has not been determined.

Accuracy of the method has not been determined.

2.5 Apparatus

2.5.1 Sample Preparation

Sample preparation apparatus requirements will depend upon the sample type under consideration and the kind of XRD analysis to be performed.

- *Mortar and Pestle:* Agate or porcelain
- *Razor Blades*
- *Sample Mill:* SPEX, Inc., freezer mill or equivalent
- *Bulk Sample Holders*
- *Silver Membrane Filters:* 25-mm diameter, 0.45-µm pore size. Sela Corp. of America, Flotronics Div., 1957 Pioneer Road, Huntingdon Valley, PA 19006
- *Microscope Slides*
- *Vacuum Filtration Apparatus:* Gelman No. 1107 or equivalent, and side-arm vacuum flask
- *Microbalance*
- *Ultrasonic Bath or Probe:* Model W140, Ultrasonics, Inc., operated at a power density of approximately 0.1 W/mL, or equivalent
- *Volumetric Flasks:* 1-L volume
- *Assorted Pipet*
- *Pipet Bulb*
- *Nonserrated Forceps*
- *Polyethylene Wash Bottle*
- *Pyrex Beakers:* 50-mL volume
- *Desiccator*
- *Fiber Storage Cassettes*
- *Magnetic Stirring Plate and Bars*
- *Porcelain Crucibles*
- *Muffle Furnace or Low Temperature Asher*

2.5.2 Sample Analysis

Sample analysis requirements include an X-ray diffraction unit, equipped with:

- *Constant Potential Generator; Voltage and mA Stabilizers*
- *Automated Diffractometer with Step-Scanning Mode*
- *Copper Target X-Ray Tube:* High intensity; fine focus, preferably
- *X-Ray Pulse Height Selector*
- *X-Ray Detector* (with high voltage power supply): Scintillation or proportional counter

- **Focusing Graphite Crystal Monochromator;** or **Nickel Filter** (if copper source is used, and iron fluorescence is not a serious problem)
- **Data Output Accessories:**
Strip Chart Recorder
Decade Scaler/Timer
Digital Printer
- **Sample Spinner** (optional)
- **Instrument Calibration Reference Specimen:** α -quartz reference crystal (Arkansas quartz standard, #180-147-00, Philips Electronics Instruments, Inc., 85 McKee Drive, Mahwah, NJ 07430) or equivalent

2.6 Reagents

2.6.1 Standard Reference Materials

The reference materials listed below are intended to serve as a guide. Every attempt should be made to acquire pure reference materials that are comparable to sample materials being analyzed.

- **Chrysotile:** UICC Canadian, or NIEHS Plastibest. (UICC reference materials available from: UICC, MRC Pneumoconiosis Unit, Llandough Hospital, Penarth, Glamorgan, CF61XW, UK)
- **Crocidolite:** UICC
- **"Amosite":** UICC
- **Anthophyllite-Asbestos:** UICC
- **Tremolite Asbestos:** Wards Natural Science Establishment, Rochester, NY; Cyprus Research Standard, Cyprus Research, 2435 Military Ave., Los Angeles, CA 90064 (washed with dilute HCl to remove small amount of calcite impurity); Indian tremolite, Rajasthan State, India
- **Actinolite Asbestos:** (Source to be determined).

2.6.2 Adhesive

Tape, petroleum jelly, etc. (for attaching silver membrane filters to sample holders).

2.6.3 Surfactant

1 Percent aerosol OT aqueous solution or equivalent.

2.6.4 Isopropanol

ACS Reagent Grade.

2.7 Procedure

2.7.1 Sampling

Samples for analysis of asbestos content shall be collected as specified in EPA Guidance Document #C0090, *Asbestos-Containing Materials in School Buildings*.¹⁰

2.7.2 Analysis

All samples must be analyzed initially for asbestos content by PLM. XRD should be used as an auxiliary method when a second, independent analysis is requested.

Note: Asbestos is a toxic substance. All handling of dry materials should be performed in an operating fume hood.

2.7.2.1 Sample Preparation

The method of sample preparation required for XRD analysis will depend on: (1) the condition of the sample received (sample size, homogeneity, particle size distribution, and overall composition as determined by PLM); and (2) the type of XRD analysis to be performed (qualitative or quantitative; thin layer or bulk).

Bulk materials are usually received as inhomogeneous mixtures of complex composition with very wide particle size distributions. Preparation of a homogeneous, representative sample from asbestos-containing materials is particularly difficult because the fibrous nature of the asbestos minerals inhibits mechanical mixing and stirring, and because milling procedures may cause adverse lattice alterations.

A discussion of specific matrix reduction procedures is given below. Complete methods of sample preparation are detailed in Sections 2.7.2.2 and 2.7.2.3. **Note:** All samples should be examined microscopically before and after each matrix reduction step to monitor changes in sample particle size distribution, composition, and crystallinity, and to ensure sample representativeness and homogeneity for analysis.

2.7.2.1.1 Milling—Mechanical milling of asbestos materials has been shown to decrease fiber crystallinity, with a resultant decrease in diffraction intensity of the specimen; the degree of lattice alteration is related to the duration and type of milling process.¹⁹⁻²² Therefore, all milling times should be kept to a minimum.

For qualitative analysis, particle size is not usually of critical importance and initial characterization of the material with a minimum of matrix reduction is often desirable to document the composition of the sample as received. Bulk samples of very large particle size (>2-3 mm) should be comminuted to ~100 μ m. A mortar and pestle can sometimes be used in size reduction of soft or loosely bound materials though this may cause matting of some samples. Such samples may be reduced by cutting with a razor blade in a mortar, or by grinding in a suitable mill (e.g., a microhammer mill or equivalent). When using a mortar for grinding or cutting, the sample should be moistened with ethanol, or some other suitable wetting agent, to minimize exposures.

For accurate, reproducible quantitative analysis, the particle size of both sample and standard materials should be reduced to ~10 μ m (see Section 2.3.3). Dry ball milling at liquid nitrogen temperatures (e.g., Spex Freezer Mill, or equivalent) for a maximum time of 10 min is recommended to obtain satisfactory particle size distributions while protecting the integrity of the crystal lattice.⁸ Bulk samples of very large particle size may require grinding in two stages for full matrix reduction to <10 μ m.^{9,10}

Final particle size distributions should always be verified by optical microscopy or another suitable method.

2.7.2.1.2. Low temperature ashing—For materials shown by PLM to contain large amounts of gypsum, cellulose, or other organic materials, it may be desirable to ash the samples prior to analysis to reduce background radiation or matrix interference. Since chrysotile undergoes dehydroxylation at temperatures between 550°C and 650°C, with subsequent transformation to forsterite,^{23,24} ashing temperatures should be kept below 500°C. Use of a low temperature ashing is recommended. In all cases, calibration of the oven is essential to ensure that a maximum ashing temperature of 500°C is not exceeded.

2.7.2.1.3 Acid leaching—Because of the interference caused by gypsum and some carbonates in the detection of asbestiform minerals by XRD (see Section 2.3.1), it may be necessary to remove these interferents by a simple acid leaching procedure prior to analysis (see Section 1.7.2.2).

2.7.2.2 Qualitative Analysis

2.7.2.2.1 Initial screening of bulk material—Qualitative analysis should be performed on a representative, homogeneous portion of the sample with a minimum of sample treatment using the following procedure:

1. Grind and mix the sample with a mortar and pestle (or equivalent method, see Section 2.7.2.1.1) to a final particle size sufficiently small (~100 μ m) to allow adequate packing into the sample holder.
2. Pack sample into a standard bulk sample holder. Care should be taken to ensure that a representative portion of the milled sample is selected for analysis. Particular care should be taken to avoid possible size segregation of the sample. (Note: Use of a back-packing method²⁵ for bulk sample

preparation may reduce preferred orientation effects.)

3. Mount the sample on the diffractometer and scan over the diagnostic peak regions for the serpentine ($\sim 7.4 \text{ \AA}$) and amphibole (8.2-8.5 \AA) minerals (see Table 2-2). The X-ray diffraction equipment should be optimized for intensity. A slow scanning speed of $1^\circ 2\theta/\text{min}$ is recommended for adequate resolution. Use of a sample spinner is recommended.
4. Submit all samples that exhibit diffraction peaks in the diagnostic regions for asbestiform minerals to a full qualitative XRD scan ($5^\circ\text{-}60^\circ 2\theta$, $1^\circ 2\theta/\text{min}$) to verify initial peak assignments and to identify potential matrix interferences when subsequent quantitative analysis is to be performed.
5. Compare the sample XRD pattern with standard reference powder diffraction patterns (i.e., JCPDS powder diffraction data³ or those of other well-characterized reference materials). Principal lattice spacings of asbestiform minerals are given in Table 2-2; common constituents of bulk insulation and wall materials are listed in Table 2-3.

2.7.2.2.2 Detection of minor or trace constituents—Routine screening of bulk materials by XRD may fail to detect small concentrations (<5 percent) of asbestos. The limits of detection will, in general, be improved if matrix absorption effects are minimized, and if the sample particle size is reduced to the optimal 1 to $10 \mu\text{m}$ range, provided that the crystal lattice is not degraded in the milling process. Therefore, in those instances where confirmation of the presence of an asbestiform mineral at very low levels is required, or where a negative result from initial screening of the bulk material by XRD (see Section 2.7.2.2.1) is in conflict with previous PLM results, it may be desirable to prepare the sample as described for quantitative analysis (see Section 2.7.2.3) and step-scan over appropriate 2θ ranges of selected diagnostic peaks (Table 2-2). Accurate transfer of the sample to the silver membrane filter is not necessary unless subsequent quantitative analysis is to be performed.

2.7.2.3 Quantitative Analysis

The proposed method for quantitation of asbestos in bulk samples is a modification of the NIOSH-recommended thin-layer method for chrysotile in air.⁵ A thick-layer or bulk

method involving pelletizing the sample may be used for semiquantitative analysis,^{7,8} however, this method requires the addition of an internal standard, use of a specially fabricated sample press, and relatively large amounts of standard reference materials. Additional research is required to evaluate the comparability of thin- and thick-layer methods for quantitative asbestos analysis.

For quantitative analysis by thin-layer methods, the following procedure is recommended:

1. Mill and size all or a substantial representative portion of the sample as outlined in Section 2.7.2.1.1.
2. Dry at 100°C for 2 hr; cool in a desiccator.
3. Weigh accurately to the nearest 0.01 mg.
4. Samples shown by PLM to contain large amounts of cellulosic or other organic materials, gypsum, or carbonates, should be submitted to appropriate matrix reduction procedures described in Sections 2.7.2.1.2 and 2.7.2.1.3. After ashing and/or acid treatment, repeat the drying and weighing procedures described above, and determine the percent weight loss, L .
5. Quantitatively transfer an accurately weighed amount (50-100 mg) of the sample to a 1-L volumetric flask with approximately 200 mL isopropanol to which 3 to 4 drops of surfactant have been added.
6. Ultrasonicate for 10 min at a power density of approximately 0.1 W/mL to disperse the sample material.
7. Dilute to volume with isopropanol.
8. Place flask on a magnetic stirring plate. Stir.
9. Place a silver membrane filter on the filtration apparatus, apply a vacuum, and attach the reservoir. Release the vacuum and add several milliliters of isopropanol to the reservoir. Vigorously hand shake the asbestos suspension and immediately withdraw an aliquot from the center of the suspension so that total sample weight, W_t , on the filter will be approximately 1 mg. Do not adjust the volume in the pipet by expelling part of the suspension; if more than the desired aliquot is withdrawn, discard the aliquot and resume the procedure with a

clean pipet. Transfer the aliquot to the reservoir. Filter rapidly under vacuum. Do not wash the reservoir walls. Leave the filter apparatus under vacuum until dry. Remove the reservoir, release the vacuum, and remove the filter with forceps. (Note: Water-soluble matrix interferences such as gypsum may be removed at this time by careful washing of the filtrate with distilled water. Extreme care should be taken not to disturb the sample.)

10. Attach the filter to a flat holder with a suitable adhesive and place on the diffractometer. Use of a sample spinner is recommended.
11. For each asbestos mineral to be quantitated, select a reflection (or reflections) that has been shown to be free from interferences by prior PLM or qualitative XRD analysis and that can be used unambiguously as an index of the amount of material present in the sample (see Table 2-2).
12. Analyze the selected diagnostic reflection(s) by step scanning in increments of $0.02^\circ 2\theta$ for an appropriate fixed time and integrating the counts. (A fixed count scan may be used alternatively; however, the method chosen should be used consistently for all samples and standards.) An appropriate scanning interval should be selected for each peak, and background corrections made. For a fixed time scan, measure the background on each side of the peak for one-half the peak-scanning time. The net intensity, I_n , is the difference between the peak integrated count and the total background count.
13. Determine the net count, I_{n0} , of the filter 2.36 \AA silver peak following the procedure in step 12. Remove the filter from the holder, reverse it, and reattach it to the holder. Determine the net count for the unattenuated silver peak, I_{n0} . Scan times may be less for measurement of silver peaks than for sample peaks; however, they should be constant throughout the analysis.
14. Normalize all raw, net intensities (to correct for instrument instabilities) by referencing them to an external standard (e.g., the 3.34 \AA peak of an α -quartz reference crystal). After each unknown is scanned, determine the net

count, I_p^0 , of the reference specimen following the procedure in step 12. Determine the normalized intensities by dividing the peak intensities by I_p^0 :

$$I_s = \frac{I_s}{I_p^0}, I_{A_0} = \frac{I_{A_0}}{I_p^0}, \text{ and } I_{\lambda_0} = \frac{I_{\lambda_0}}{I_p^0}$$

2.8 Calibration

2.8.1 Preparation of Calibration Standards

1. Mill and size standard asbestos materials according to the procedure outlined in Section 2.7.2.1.1. *Equivalent, standardized matrix reduction and sizing techniques should be used for both standard and sample materials.*
2. Dry at 100°C for 2 hr; cool in a desiccator.
3. Prepare two suspensions of each standard in isopropanol by weighing approximately 10 and 50 mg of the dry material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L volumetric flask with approximately 200 mL isopropanol to which a few drops of surfactant have been added.
4. Ultrasonicate for 10 min at a power density of approximately 0.1 W/mL to disperse the asbestos material.
5. Dilute to volume with isopropanol.
6. Place the flask on a magnetic stirring plate. Stir.
7. Prepare, in triplicate, a series of at least five standard filters to cover the desired analytical range, using appropriate aliquots of the 10 and 50 mg/L suspensions. For each standard, mount a silver membrane filter on the filtration apparatus. Place a few mL of isopropanol in the reservoir. Vigorously hand shake the asbestos suspension and immediately withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension; if more than the desired aliquot is withdrawn, discard the aliquot and resume the procedure with a clean pipet. Transfer the aliquot to the reservoir. Keep the tip of the pipet near the surface of the isopropanol. Filter rapidly under vacuum. Do not wash the sides of the reservoir. Leave the vacuum on for a time sufficient to dry the filter. Release the vacuum and remove the filter with forceps.

2.8.2 Analysis of Calibration Standards

1. Mount each filter on a flat holder. Perform step scans on selected diagnostic reflections of the standards and reference specimen using the procedure outlined in Section 2.7.2.3, step 12, and the same conditions as those used for the samples.
2. Determine the normalized intensity for each peak measured, I_{sio}^0 , as outlined in Section 2.7.2.3, step 14.

2.9 Calculations

For each asbestos reference material, calculate the exact weight deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w , of each standard. Prepare a calibration curve by regressing I_{sio}^0 on w . Poor reproducibility (± 15 percent RSD) at any given level indicates problems in the sample preparation technique, and a need for new standards. The data should fit a straight line equation.

Determine the slope, m , of the calibration curve in counts/microgram. The intercept, b , of the line with the I_{sio}^0 axis should be approximately zero. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

Using the normalized intensity, I_{A_0} , for the attenuated silver peak of a sample, and the corresponding normalized intensity from the unattenuated silver peak, I_{λ_0} , of the sample filter, calculate the transmittance, T , for each sample as follows:^{26,27}

$$T = \frac{I_{A_0}}{I_{\lambda_0}}$$

Determine the correction factor, $f(T)$, for each sample according to the formula:

$$f(T) = \frac{-R(\ln T)}{1-T^R}$$

where

$$R = \frac{\sin \theta_{A_0}}{\sin \theta_s}$$

θ_{A_0} = angular position of the measured silver peak (from Bragg's Law), and
 θ_s = angular position of the diagnostic asbestos peak.

Calculate the weight, W_s , in micrograms, of the asbestos material analyzed for in each sample, using the appropriate calibration data and absorption corrections:

$$W_s = \frac{I_s f(T) - b}{m}$$

Calculate the percent composition, P_s , of each asbestos mineral analyzed for in the parent material, from the total sample weight, W_T , on the filter:

$$P_s = \frac{W_s (1 - 0.01L)}{W_T} \times 100$$

where

P_s = percent asbestos mineral in parent material,

W_s = mass of asbestos mineral on filter, in μg ;

W_T = total sample weight on filter, in μg ;

L = percent weight loss of parent material on ashing and/or acid treatment (see Section 2.7.2.3).

2.10 References

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Table 2-1. The asbestos minerals and their nonasbestiform analogs.

Asbestiform	Nonasbestiform
Serpentine	
Chrysotile	Antigorite, lizardite
Amphibole	
Anthophyllite asbestos	Anthophyllite
Cummingtonite-grunerite asbestos ("Amosite")	Cummingtonite-grunerite
Crocidolite	Riebeckite
Tremolite asbestos	Tremolite
Actinolite asbestos	Actinolite

Table 2-2. Principal lattice spacings of asbestiform minerals*

Minerals	Principal d-spacings (Å) and relative intensities			JCPDS Powder diffraction file ^c number
Chrysotile	7.37 ₁₀₀	3.65 ₇₀	4.57 ₅₀	21-543 ^c
	7.36 ₁₀₀	3.66 ₈₀	2.45 ₆₅	25-645
	7.10 ₁₀₀	2.33 ₈₀	3.55 ₇₀	22-1162 (theoretical)
"Amosite"	8.33 ₁₀₀	3.06 ₇₀	2.756 ₇₀	17-745 (nonfibrous)
	8.22 ₁₀₀	3.060 ₈₅	3.25 ₇₀	27-1170 (UICC)
Anthrophyllite	3.05 ₁₀₀	3.24 ₆₀	8.26 ₅₅	9-455
	3.06 ₁₀₀	8.33 ₇₀	3.23 ₅₀	16-401 (synthetic)
Actinolite	2.72 ₁₀₀	2.54 ₁₀₀	3.40 ₈₀	25-157
Crocidolite	8.35 ₁₀₀	3.10 ₅₅	2.720 ₃₅	27-1415 (UICC)
Tremolite	8.38 ₁₀₀	3.12 ₁₀₀	2.705 ₉₀	13-437 ^c
	2.706 ₁₀₀	3.14 ₉₅	8.43 ₄₀	20-1310 ^c (synthetic)
	3.13 ₁₀₀	2.706 ₈₀	8.44 ₄₀	23-666 (synthetic mixture with richterite)

*This information is intended as a guide, only. Complete powder diffraction data including mineral type and source, should be referred to, to ensure comparability of sample and reference materials where possible. Additional precision XRD data on amosite, crocidolite, tremolite, and chrysotile are available from the U.S. Bureau of Mines, Reference 4.

^bFrom Reference 3

^cFibrosity questionable

Table 2-3. Common constituents in insulation and wall materials (from Ref. 10)

A. Insulation materials	B. Spray finishes or paints
Chrysotile	Bassanite
"Amosite"	Carbonate minerals (calcite, dolomite, vaterite)
Crocidolite	Talc
*Rock wool	Tremolite
*Slag wool	Anthophyllite
*Fiber glass	Serpentine (including chrysotile)
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	"Amosite"
Vermiculite (micas)	Crocidolite
*Perlite	*Mineral wool
Clays (kaolin)	*Rock wool
*Wood pulp	*Slag wool
*Paper fibers (talc, clay, carbonate fillers)	*Fiber glass
Calcium silicates (synthetic)	Clays (kaolin)
Opaques (chromite, magnetite inclusions in serpentine)	Micas
Hematite (inclusions in "amosite")	Chlorite
Magnesite	Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
*Diatomaceous earth	Quartz
	*Organic binders and thickeners
	Hydromagnesite
	Wollastonite
	Opaques (chromite, magnetite inclusions in serpentine)
	Hematite (inclusions in "amosite")

*Amorphous materials--contribute only to overall scattered radiation and increased background radiation.

Table 2-4. Interferences in XRD analysis of asbestiform minerals

Asbestiform mineral	Primary diagnostic peaks (approximate d-spacings in Å)	Interference
Serpentine		
Chrysotile	7.4	Nonasbestiform serpentines (antigorite, lizardite)
		Chlorite
		Kaolinite
		Gypsum
	3.7	Nonasbestiform serpentines, (antigorite, lizardite)
		Chlorite
		Halloysite
		Cellulose
Amphibole		
"Amosite"	3.1	Nonasbestiform amphiboles (cummingtonite-grunerite, anthophyllite, riebeckite, tremolite)
Anthophyllite		Mutual interferences
Crocidolite		Carbonates
Tremolite		Talc
	8.3	Nonasbestiform amphiboles (cummingtonite, grunerite, anthophyllite, riebeckite, tremolite)
		Mutual interferences

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati, OH 45268

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objectionable and the grounds for the objections. If a hearing is requested, the objections must state the issues for the hearing and the grounds for the objections. A hearing will be granted if the objections are supported by grounds legally sufficient to justify the relief sought.

The Office of Management and Budget has exempted this rule from the requirements of section 3 of Executive Order 12291.

(Sec. 408(e), 68 Stat. 514 (21 U.S.C. 346a(e)))

List of Subjects in 40 CFR Part 180

Administrative practice and procedure, Agricultural commodities, Pesticides and pests.

Dated: August 18, 1982.

Edwin L. Johnson,

Director, Office of Pesticide Programs.

PART 180—TOLERANCES AND EXEMPTIONS FROM TOLERANCES FOR PESTICIDE CHEMICALS IN OR ON RAW AGRICULTURAL COMMODITIES

Therefore, 40 CFR Part 180 is amended by adding a new § 180.1076 to read as follows:

§ 180.1076 Viable spores of the microorganism *Bacillus popilliae*; exemption from the requirement of a tolerance.

(a) For the purposes of this section the microbial insecticide for which exemption from the requirement of a tolerance is being established shall have the following specifications:

(1) The microorganism shall be an authentic strain of *Bacillus popilliae* conforming to the morphological and biochemical characteristics of *Bacillus popilliae* as described in Bergey's Manual of Determinative Bacteriology, Eighth Edition.

(2) Spore preparations of *Bacillus popilliae* shall be produced by an extraction process from diseased Japanese beetles, and may contain a small percentage of the naturally occurring milky disease bacterium *Bacillus lentimorbus*.

(3) Each lot of spore preparation, prior to the addition of other materials, shall be tested by subcutaneous injection of at least 1 million spores into each of five laboratory test mice weighing 17 grams to 23 grams. Such test shall show no evidence of infection of injury in the test animals when observed for 7 days following injection.

(b) Exemption from the requirement of a tolerance is established for residues of the microbial insecticide *Bacillus popilliae*, as specified in paragraph (a) of this section in or on pasture and rangeland forage when it is applied to

growing crops in accordance with good agricultural practices.

(FR Doc. 22678 Filed 8-31-82; 8:45 am)

BILLING CODE 6560-50-M

40 CFR Part 763

(OPTS 61004C; TSH-FRL 2198-8)

Asbestos; Friable Asbestos-Containing Materials in Schools: Identification and Notification; Correction

AGENCY: Environmental Protection Agency (EPA).

ACTION: Rule, Correction.

SUMMARY: EPA issued a regulation requiring the inspection of public and private elementary and secondary schools in the United States to identify friable asbestos-containing building materials. Each local education agency is required to inspect all areas of each school, take samples of each distinct type of friable material found, and have those samples analyzed for their asbestos content using polarized light microscopy (PLM) augmented by X-ray diffraction where necessary. This correction clarifies the rule to indicate that EPA will find it acceptable for laboratories analyzing samples under this rule to estimate the amount of asbestos in the bulk samples using methods equivalent to the point counting procedure contained in the "Interim Method for Determination of Asbestiform Minerals in Bulk Insulation Samples," published as Appendix A to the rule.

EFFECTIVE DATE: Effective on June 28, 1982.

FOR FURTHER INFORMATION CONTACT: Douglas G. Bannerman, Acting Director, Industry Assistance Office (TS-799), Office of Toxic Substances, Environmental Protection Agency, Rm. E-511, 401 M St., SW, Washington, D.C. 20460. Toll free: (800-424-9035). In Washington, D.C.: (554-1404). Outside the USA: (Operator-202-554-1404).

SUPPLEMENTARY INFORMATION: EPA issued a regulation published in the Federal Register of May 27, 1982 (47 FR 23360), which requires the inspection of all public and private elementary and secondary schools for friable asbestos-containing materials in school buildings. Samples of friable materials must be analyzed using PLM, supplemented where necessary by X-ray diffraction, in accordance with the "Interim Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples," found in Appendix A of the rule. The Interim Method provides information for the proper identification of asbestos in

bulk samples and includes procedures for estimating the amount of asbestos present in bulk samples.

Paragraph 1.7.2.4 of Appendix A of the rule was intended to provide for a point counting procedure or an equivalent estimation method for determining the amount of asbestos in bulk samples. The phrase "or an equivalent estimation method" was inadvertently omitted from the first sentence of paragraph 1.7.2.4 of the Appendix.

Questions concerning equivalent estimation methods should be directed to EPA's toll-free, technical assistance number (800-334-8571, extension 6741).

Appendix A—Interim Method for the Determination of Asbestos in Bulk Insulation

§ 1.7.2.4 [Corrected]

In FR Doc. 82-14477 appearing on page 23362, in the first column, the regulatory text under 1.7.2.4, *Quantitation of Asbestos Content*, is corrected by adding the phrase "or an equivalent estimation method" in line 2, at the end of the first sentence.

Dated: August 24, 1982

Edwin L. Johnson,

Acting Assistant Administrator for Pesticides and Toxic Substances.

(FR Doc. 82-24741 Filed 8-31-82; 8:45 am)

BILLING CODE 6560-50-M

DEPARTMENT OF HEALTH AND HUMAN SERVICES

Health Care Financing Administration

42 CFR Part 421

Medicare Program; Assignment and Reassignment of Home Health Agencies to Designated Regional Intermediaries

AGENCY: Health Care Financing Administration (HCFA), HHS.

ACTION: Final rule.

SUMMARY: We are modifying Medicare regulations to require that all freestanding home health agencies serviced by a nominated intermediary be serviced by a regional intermediary designated by HCFA.

These regulations implement section 1816(c)(4) of the Social Security Act (as added by section 930(o) of the Omnibus Reconciliation Act of 1980, Pub. L. 96-499), which requires the Secretary to designate regional agencies or organizations to perform intermediary functions for home health agencies.

EFFECTIVE DATE: These regulations are effective October 1, 1982.

SECTION C

VOLATILE ORGANICS IN SOIL/SEDIMENT SAMPLES BY
GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS):
USATHAMA CERTIFIED METHOD N9 FOR UBTL;
AND USATHAMA CERTIFIED METHOD K9 FOR CAL

DEVELOPED FROM
EPA METHOD 8240, SW-8846, 2ND ED., JULY 1982

USATHAMA CERTIFIED METHOD N9 FOR UBTL

VOLATILE ORGANICS IN SOIL/SEDIMENT SAMPLES
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) METHOD A

1. APPLICATION

This method is applicable to the semiquantitative determination of the following compounds in environmental soil/sediment samples by GC/MS:

Benzene	Methylene chloride
Carbon tetrachloride	Tetrachloroethene
Chlorobenzene	Toluene
Chloroform	1,1,1-Trichloroethane
1,1-Dichloroethane	1,1,2-Trichloroethane
1,2-Dichloroethane	Trichloroethene
Dibromochloropropane (DBCP)	m-Xylene
Dicyclopentadiene	o-Xylene
Bicycloheptadiene	p-Xylene
trans-1,2,-Dichloroethene	Methylisobutylketone (MIBK)
Ethylbenzene	Dimethyldisulfide (DMDS)

A. TESTED CONCENTRATION RANGE

The tested concentration ranges of the compounds examined in "standard soil" are as follows:

<u>Analyte</u>	<u>Tested Concentration Range (ug/g)*</u>
Ethylbenzene	0.25 to 25
Benzene	0.25 to 25
MIBK	0.25 to 25
DMDS	0.25 to 25
1,1-Dichloroethane	0.25 to 25
1,2-Dichloroethane	0.25 to 25
1,1,1-Trichloroethane	0.25 to 25
1,1,2-Trichloroethane	0.25 to 25
Methylene chloride	0.25 to 25

<u>Analyte</u>	<u>Tested Concentration Range (ug/g)*</u>
Chloroform	0.25 to 25
Carbon tetrachloride	0.25 to 25
trans-1,2,-Dichloroethene	0.25 to 25
Toluene	0.25 to 25
Chlorobenzene	0.25 to 25
Tetrachloroethene	0.25 to 25
Trichloroethene	0.25 to 25
m-Xylene	0.25 to 25
o- and/or p-Xylenes†	0.5 to 50
DBCP	0.25 to 25
Dicyclopentadiene	0.27 to 26.5
Bicycloheptadiene	0.25 to 25
1,2,-Dichloroethane-D ₄	0.25 to 25
Methylene chloride-D ₂	0.25 to 25
Ethylbenzene-D ₁₀	0.25 to 25

*ug/g = micrograms per gram.

†Ortho - and para - (o- and p-) xylene coelute under the GC conditions specified in this method. The tested concentration range given represents the sum of the individual tested concentration range for each specific isomer.

B. SENSITIVITY

The extracted ion current area count responses at the "standard soil" detection limits (Sec. 1.C) are:

<u>Analyte</u>	<u>Quantitation Ion</u>	<u>Area Counts</u>	<u>Retention Time*</u>	<u>Relative Retention Time (RRT)</u>
Ethylbenzene	106	1,700	31:22	1.487
Benzene	78	13,000	20:26	0.968
MIBK	58	2,400	23:17	1.103
DMDS	94	190,000	19:10	0.908
1,1-Dichloroethane	63	38,000	12:58	0.615

<u>Analyte</u>	<u>Quantitation Ion</u>	<u>Area Counts</u>	<u>Retention Time*</u>	<u>Relative Retention Time (RRT)</u>
1,2-Dichloroethane	62	8,200	15:15	0.723
1,1,1-Trichloroethane	97	3,300	16:28	0.780
1,1,2-Trichloroethane	97	4,000	20:23	0.966
Methylene chloride	84	33,000	8:29	0.402
Chloroform	83	4,600	14:23	0.682
Carbon tetrachloride	117	1,900	16:50	0.798
Trans-1,2,-Dichloroethene	96	21,000	13:56	0.660
Toluene	92	8,500	26:41	1.265
Chlorobenzene	112	15,000	28:07	1.333
Tetrachloroethene	164	3,800	25:07	1.190
Trichloroethene	130	7,100	19:49	0.939
m-Xylene	91	27,000	38:50	1.840
o- and/or p-Xylene	91	186,100	40:37	1.925
DBCP	157	1,800	31:10	1.477
Dicyclopentadiene	66	3,500	27:33	1.306
Bicycloheptadiene	91	11,000	17:38	0.836
1,2-Dichloroethane-D ₄	67	1,300	15:06	0.716
Methylene chloride-D ₂	53	1,000	8:26	0.400
Ethylbenzene-D ₁₀	98	14,000	30:57	1.467
1,2-Dibromoethane-D ₄	111	Internal Standard	21:06	1.00
Chlorobenzene-D ₅		†		

*minutes:seconds

†UBTL Internal Standard (not characterized, used to monitor column and instrument performance in the later part of the run, not used for quantitation).

C. DETECTION LIMITS

The detection limits in "standard soil", calculated according to the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) detection limit program with 90-percent confidence limits (USATHAMA, 1982), are:

<u>Analyte</u>	<u>Detection Limit ($\mu\text{g/g}$)</u>	<u>Range ($\mu\text{g/g}$)</u>
Ethylbenzene	0.4	0.4-25
Benzene	0.3	0.3-25
MIBK	0.7	0.7-25
DMDS	20	20-25
1,1-Dichloroethane	2	2-25
1,2-Dichloroethane	0.6	0.6-5
1,1,1-Trichloroethane	0.4	0.4-10
1,1,2-Trichloroethane	0.4	0.4-25
Methylene chloride	2	2-25
Chloroform	0.3	0.3-5
Carbon tetrachloride	0.3	0.3-10
trans-1,2,-Dichloroethene	2	2-25
Toluene	0.3	0.3-25
Chlorobenzene	1	1-10
Tetrachloroethene	0.3	0.3-25
Trichloroethene	0.5	0.5-25
m-Xylene	0.8	0.8-10
o-and/or p-Xylene	5	5-50
DBCP	2	2-25
Dicyclopentadiene	0.7	0.7-25
Bicycloheptadiene	0.4	0.4-10
1,2,-Dichloroethane-D ₄	0.3	0.3-25
Methylene chloride-D ₂	0.4	0.4-25
Ethylbenzene-D ₁₀	0.3	0.3-25

D. INTERFERENCES

No interferences were encountered in "standard soil" samples. Precautions described in Test Method 624 [U.S. Environmental Protection Agency (EPA), 1982] must be taken to prevent contamination artifacts.

Two of the tested analytes coelute under the GC conditions specified in this method. These compounds are the isomers

o-xylene and p-xylene, which cannot be differentiated by GC/MS. For the purpose of this method, these two compounds are reported as o- and/or p-xylene.

E. ANALYSIS RATE

After instrument calibration, one analyst can analyze five samples in a 9-hour day.

2. CHEMISTRY

A. CHEMICAL ABSTRACT SERVICE (CAS) REGISTRY NUMBERS

<u>Analyte</u>	<u>CAS Registry Number</u>
Ethylbenzene	100-41-4
Benzene	71-43-2
MIBK	108-10-1
DMDS	624-92-0
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Methylene chloride	75-09-2
Chloroform	67-66-3
Carbon tetrachloride	56-23-5
trans-1,2,-Dichloroethene	156-60-5
Toluene	108-88-3
Chlorobenzene	108-90-7
Tetrachloroethene	127-18-4
Trichloroethene	79-01-4
m-Xylene	108-38-3
o-Xylene	95-47-6
p-Xylene	106-42-3
DBCP	96-12-8
Dicyclopentadiene	77-73-60
Bicycloheptadiene	121-46-0

B. CHEMICAL REACTIONS

In the laboratory, the soil sample is placed into a vial containing 10 milliliters (mL) of methanol. Prior to analysis, the vial is spiked with the surrogate compounds. Then, 0.02 mL are removed from the vial, transferred to a specially designed purging chamber containing 5.0 mL of organic-free water, and spiked with two internal standards. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column, where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a GC column. The GC is temperature programmed to separate the purgeables, which are then detected with an MS.

3. APPARATUS**A. INSTRUMENTATION**

A Finnigan 1020B GC/MS with electron impact ionization source.

B. GC/MS PARAMETERS, HARDWARE, GLASSWARE, AND REAGENTS

EPA Method 624 (EPA, 1982) for purgeables, attached to this method (Att. 1), describes the recommended GC/MS parameters, hardware, glassware, and reagents used in this procedure.

The actual GC conditions are:

Column:	1% SP-1000 on 60/80 mesh Carbo pack B
Length:	6 feet, glass
Inside diameter:	2 millimeters x 1/4 inch
Temperature Program:	Hold at 45 degrees Celsius (°C) for three minutes, then to 220 °C programmed at 8 °C per min.
Run Time:	43 minutes, 12 seconds (850 scans acquired)
Carrier Gas:	Helium (research grade)
Injector Temperature:	220 °C

A reconstructed total ion current profile of the 160 µg/L calibration standard is attached to this method.

C. SAMPLING CONTAINER PREPARATION

The sample container is an amber glass 40 mL VOA vial with a Teflon lined cap. The Teflon lined cap is cleaned by shaking methanol in a capped vial, removing the cap and air drying. The vial is cleaned by rinsing with methanol, drying at 105° overnight, capping and cooling.

D. METHANOL PREPARATION

The methanol (Fisher Scientific, HPLC grade) is warmed to 40 °C on a stirring hot plate and purged with a continuous stream of high-purity helium for a minimum of 16 hours. It is recommended that each batch of methanol be prescreened prior to utilization to verify that significant contamination is not present. Helium is forced through a Teflon tube and exits a stainless steel frit as a fine stream of bubbles. The helium flow rate is 45 mL per min. The reagent bottle is capped with aluminum foil. The aluminum foil is secured sufficiently to allow the Teflon tube to enter the reagent bottle and to allow the helium to exit. The methanol purging procedure reduced the amount of methylene chloride and other compounds present in the methanol. However, the methylene chloride could not be reduced to an insignificant level by extending the purging time and consequently remained as a contaminant in the extraction solvent.

E. SAMPLING PROCEDURE

In the laboratory, a clean, prelabeled sample container is opened and tared. Ten grams (g) of soil sample are quickly added to the sampling container, after which 10 mL of clean methanol are added; the container is then resealed.

4. STANDARDSA. INITIAL INSTRUMENT CALIBRATION STANDARDS

1. Eleven stock solutions of the target volatiles and deuterated surrogate compounds were prepared by weighing or using an appropriate calibrated syringe. The appropriate amounts of each SARM compound are introduced into 10-mL volumetric flasks containing 5 mL of methanol. The solutions were numbered consecutively, beginning with VS SARM 1 (VSS1); the dilute surrogate compounds are identified in a similar manner. Solutions were prepared with microliter syringes and "to contain" pipets, which were rinsed several times with methanol after addition to the volumetric flask. As soon as all of the compounds for a particular stock solution were added to the volumetric flask, the solution was diluted to the 10-mL mark with methanol. Table 1 lists the group of compounds in each stock solution, the density of the compounds, the volume or weight of each compound added, and the final concentrations.
2. A stock calibration solution consisting of two internal standards was made by adding 92 microliters (μ L) of 1,2-dibromoethane-(D4) (MSD Isotopes, St. Louis, MO) to 5 mL of methanol in a 10-mL volumetric flask and 200 mg chlorobenzene-(D5) (Aldrich Chemical Co.) and diluting to volume with methanol. The concentration of the stock calibration internal standards was 20 milligrams per milliliter (mg/mL). The density of the 1,2-dibromoethane-(D4) was 2.18 grams per milliliter (g/mL).

A dilute stock internal standard solution was prepared by placing 20 μ L of the stock calibration internal standard solution into 5 mL of methanol in a 10-mL volumetric flask and diluting to volume with methanol.

The concentration of dilute stock internal standard calibration solution was 40 micrograms per milliliter ($\mu\text{g/mL}$) for both internal standards.

3. Prepare the dilute composite target compound calibration standard solutions using disposable micropipettes or equivalent, 10-mL volumetric flasks, and 1-mL glass crimp-top septum vials:
 - a. Place 125 μL each of VSS1 through VSS10 into a 5-mL volumetric flask containing 2.5 mL of methanol and dilute to volume with methanol to give a dilute composite calibration standard solution designated VSSB1. The concentration of all analytes in VSSB1 is approximately 50 $\mu\text{g/mL}$. A separate dilute calibration standard solution is prepared for DBCP by placing 125 μL of VSS11 into a 5-mL volumetric flask containing 2.5 mL of methanol and diluting to volume with methanol to give a solution (VSSB2) with a DBCP concentration of 50 $\mu\text{g/mL}$. This solution is made up fresh daily using a new VSS2 solution prepared the same day (containing DMDS). To clarify this procedure note that neat DMDS was weighed out and a fresh stock solution (VSS2) is prepared daily as well as the subsequent dilution to VSSB1.
 - b. Place 200 μL of VSSB1 into a 1 mL volumetric flask and bring to volume with methanol to give a dilute composite calibration solution VSSC1. The concentration of all analytes in VSSC1 is approximately 10 $\mu\text{g/mL}$. Similarly, a separate dilute calibration standard solution of DBCP is prepared by placing 200 μL of VSSB2 into a 1 mL volumetric flask and bringing to volume with methanol to give a solution (VSSC2) with a DBCP concentration of 10 $\mu\text{g/mL}$.

- c. Place 100 μ L of VSSC1 into a 1 mL volumetric flask and bring to volume with methanol to give a dilute composite calibration standard solution VSSD1. The concentration of all analytes in VSSD1 is approximately 1 μ g/mL. Similarly, a separate dilute calibration standard solution of DBCP is prepared by placing 100 μ L of VSSC2 into a 1 mL volumetric flask and bringing to volume with methanol to give a solution (VSSD2) with a DBCP concentration of 1 μ g/mL.

B. DAILY INSTRUMENT CALIBRATION STANDARDS

1. Prepare a daily SARM calibration standard (VSSD) as follows:
 - a. Prepare the daily SARM calibration standard VSSD by pipetting 200 μ L of each of VSS1 through VSS11 into a 10-mL volumetric flask containing 5 mL of methanol and diluting to volume with methanol. The concentration of all SARM analytes in VSSD is approximately 40 μ g/mL (Table 2).

C. INITIAL INSTRUMENT CALIBRATION

The following calibration standards were analyzed to calibrate the linear range of the system for each SARM compound. In each case, 5 mL of organic-free water are spiked with aliquots of the indicated composite SARM calibration solution and internal standards and then purged and analyzed. The amount of methanol in each calibration standard was kept uniform regardless of the amount of standard spiked. A total of 45 mL of methanol was added to each standard; 5 μ L from the internal standard spike, and from 5 to 20 μ L from the standard spiking solution. The difference was made up with the methanol solvent. The area

of the quantitation ion for each standard compound divided by the area of the internal standard (quantitation ion m/e 111) is plotted against the micrograms of each standard compound purged and analyzed. The correlation coefficient of the linear regression plot of each of these standard compounds was 0.996 or greater over the range calibrated.

1. SARM Calibration Standard No. 1 (Blank)

Composed of 40 μL of methanol and 5.0 μL of the 40- $\mu\text{g}/\text{mL}$ dilute stock internal standard calibration solution only.

2. SARM Calibration Standard No.2 [1 microgram per liter ($\mu\text{g}/\text{l}$)]

Composed of 5.0 μL each of the 1- $\mu\text{g}/\text{mL}$ dilute composite VSSD1 and VSSD2 target compound calibration solutions, 5.0 μL of the 40- $\mu\text{g}/\text{mL}$ dilute stock internal standard calibration solution, and 30 μL of reagent methanol.

3. SARM Calibration Standard No. 3 (2 $\mu\text{g}/\text{l}$)

Composed of 10 μL each of the 1- $\mu\text{g}/\text{mL}$ dilute composite VSSD1 and VSSD2 target compound calibration solutions, 5.0 μL of the 40- $\mu\text{g}/\text{mL}$ dilute stock internal standard calibration solution, and 20 μL of reagent methanol.

4. SARM Calibration Standard No. 4 (4 $\mu\text{g}/\text{l}$)

Composed of 20.0 μL each of the 1- $\mu\text{g}/\text{mL}$ dilute composite VSSD1 and VSSD2 target compound calibration solutions and 5.0 μL of the 40- $\mu\text{g}/\text{mL}$ dilute stock internal standard calibration solution.

5. SARM Calibration Standard No. 5 (10 $\mu\text{g}/\text{l}$)

Composed of 5.0 μL each of the 10- $\mu\text{g}/\text{mL}$ dilute composite VSSC1 and VSSC2 target compound calibration solutions, 5.0 μL of the 40- $\mu\text{g}/\text{mL}$ dilute stock internal standard calibration solution, and 30 μL of reagent methanol.

6. SARM Calibration Standard No. 6 (20 µg/l)

Composed of 10.0 µL each of the 10-µg/mL dilute composite VSSC1 and VSSC2 target compound calibration solutions, 5.0 µL of the 40-µg/mL dilute stock internal standard calibration solution, and 20 µL of reagent methanol.

7. SARM Calibration Standard No. 7 (40 µg/l)

Composed of 20.0 µL each of the 10-µg/mL dilute composite VSSC1 and VSSC2 target compound calibration solutions and 5.0 µL of the 40-µg/mL dilute stock internal standard calibration solution.

8. SARM Calibration Standard No. 8 (100 µg/l)

Composed of 10 µL each of the 50-µg/mL dilute composite VSSB1 and VSSB2 target compound calibration solutions, 5.0 µL of the 40-µg/mL dilute stock internal standard calibration solution, and 20 µL of reagent methanol.

9. SARM Calibration Standard No. 9 (160 µg/l)

Composed of 16.0 µL each of the 50-µg/mL dilute composite VSSB1 and VSSB2 target compound calibration solutions, 5.0 µL of the 40-µg/mL dilute stock internal standard calibration solution, and 8 µL of reagent methanol.

D. DAILY INSTRUMENT CALIBRATION

Since initial calibration established that the instrument is linear over the certified range, it is only necessary to verify by use of a 1-point calibration standard run daily that the instrument response has not drifted significantly (i.e., the response factors of the surrogate compounds have not changed by more than 25 percent from those obtained during initial calibration). This 1-point daily calibration

standard is used to establish daily response factors for each of the certified analytes. The standards utilized for these daily calibrations are the dilute stock internal standard calibration solution (as prepared in Sec. 4.A.2) and the VSSD daily calibration standard (as prepared in Sec. 4.B.1.a).

1. Analysis of the VSSD Daily Calibration Standard

Spike 5.0 μL of the VSSD daily calibration standard and 5.0 μL of the dilute stock internal standard calibration solution into 5.0 mL of organic-free water and analyze by purge-and-trap analysis, as described in Sec. 11 of Att. 1 (EPA Test Method 624). This corresponds to purging and analyzing 0.2 μg of each of the SARM compounds and the internal standard compounds.

E. CONTROL SPIKES

1. The solutions used for control spiking were the dilute composite solutions VSSB1 and VSSB2 as prepared in Sec. 4.A.3.a.
2. The control spikes were prepared by placing 10 g of "standard soil" (uncontaminated natural soil obtained from the Rocky Mountain Arsenal, Denver, CO, area) into a 40 mL amber vial, then adding the appropriate amounts of spiking solution and methanol as shown in Table 3. The spiked vials are capped and mixed by inverting the vials a minimum of 20 times.

5. PROCEDURE

A. ANALYSIS OF CERTIFICATION CONTROL SPIKES ONLY

1. Using a syringe, remove 0.02 mL from the control spike sample vial as prepared in Table 3 and spike it into 5.0 mL of organic-free water contained in the sample syringe.

2. Spike 5 μ L of the dilute stock internal standard calibration solution (as prepared in Sec. 4.A.2) into the sample syringe.
3. Transfer the spiked 5 mL of sample contained in the sample syringe to the purging device (see Fig.1 of Att. 1).
4. Purge and analyze the sample as described in Sec. 11 of Att. 1.

B. ANALYSIS OF ENVIRONMENTAL SAMPLES

1. Prepare stock surrogate solutions (to be used in the analysis of environmental samples) as follows:
 - a. Place 1,000 mg of 1,2,-dichloroethane- d_4 into a 10-mL volumetric flask containing 5 mL of methanol and dilute to volume with methanol to produce a 100,000- μ g/mL 1,2,-dichloroethane- d_4 stock surrogate solution (designated stock surrogate solution 12DCD4).
 - b. Place 1,000 mg of methylene chloride- d_2 into a 10-mL volumetric flask containing 5 mL of methanol and dilute to volume with methanol to produce a 100,000- μ g/mL methylene chloride- d_2 stock surrogate solution (designated stock surrogate solution CD2CL2).
 - c. Place 1,000 mg of ethylbenzene- d_{10} into a 10-mL volumetric flask containing 5 mL of methanol and dilute to volume with methanol to produce a 100,000- μ g/mL ethylbenzene- d_{10} stock surrogate solution (designated stock surrogate solution C8D10).

2. Prepare the VS2 surrogate spike solution by taking two mL of each of the three stock surrogate solutions prepared in Sec. 5.B.1 and diluting to 10 mL with methanol. (Note: The aliquots are added to 10-mL volumetric flasks containing 3 mL of methanol to minimize evaporative losses during the transfer. After addition of all three aliquots, the solution is diluted to the 10-mL mark with methanol). Surrogate spike solution VS2 contains each of the three surrogates at a concentration of 20 mg/mL.
3. Analyze 4-bromofluorobenzene (BFB) and adjust the tune of the mass spectrometer as required to the key ion abundance criteria of EPA Method 624.
4. Analyze a water blank consisting of 5 mL of organic-free water spiked with 5 μ L of the dilute stock internal standard calibration solution (as prepared in Sec. 4.A.2). The internal standard is added to a 5-mL syringe containing 5 mL of organic-free water and then transferred to the purging device. The water blank is then purged and analyzed according to Sec. 11 of Att. 1.
5. Analyze a method blank (to check for contamination of the reagents used) as follows:
 - a. Place 10 g of standard soil in a vial with 10 mL of methanol and spike with 5 μ L of the VS2 surrogate spike solution. The vial is quickly sealed and mixed on a wrist action shaker for four hours.
 - b. Remove 20 μ L of methanol from the vial with a syringe and transfer to a syringe containing 5 mL of organic-free water.

- c. Add 5 μ L of the dilute stock internal standard calibration solution (as prepared in Sec. 4.A.2) into the 5-mL syringe.
 - d. Transfer entire contents of the syringe into the purging device; purge and analyze as described in Sec. 11 of Att. 1.
6. Analyze the VSSD daily calibration standard as described in Sec. 4.D.1.
7. Analyze soil samples as follows:
- a. A 10-g sample of soil is placed in a vial with 10 mL of methanol and spiked with 5 μ L of the VS2 surrogate spike solution, quickly sealed, and mixed on a wrist action shaker for 4 hours.
 - b. Using a syringe, remove 20 μ L of the methanol from the vial and transfer to a syringe containing 5 mL of organic-free water.
 - c. Add 5 μ L of the dilute stock internal standard calibration solution (as prepared in Sec. 4.A.2) into the 5-mL syringe.
 - d. Transfer entire contents of the syringe into the purging device; purge and analyze as described in Sec. 11 of Att.1.

6. CALCULATIONS

A. DOCUMENTED COMPOUNDS

- 1. The following calculations are performed to determine the concentrations of compounds for which method documentation has been performed:

$$\text{Concentration (micrograms purged)} = (A_s C_{is}) / (A_{is}) (RF)$$

where: A_s = Area of the characteristic ion for the analyte to be measured,
 A_{is} = Area of the characteristic ion for the internal standard,
 C_{is} = Micrograms of the internal standard purged, and
 RF = Response factor calculated from the daily calibration standard.

The response factor (RF) for each compound is calculated as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where: A_s = Area of the characteristic ion for the analyte to be measured (this area is corrected for any trace contamination found in the water blank),
 A_{is} = Area of the characteristic ion for the internal standard,
 C_{is} = Micrograms of the internal standard purged, and
 C_s = Micrograms of the parameter to be measured purged.

2. The concentration of each documented compound in the sample, in micrograms per gram (wet weight) basis, is calculated as follows:

$$\frac{(\text{micrograms purged} - \text{micrograms purged in method blank}) \frac{10 \text{ ml}}{0.02 \text{ ml}}}{\text{Weight of soil sample in vial in grams}}$$

3. The concentration, in micrograms per gram (wet weight) basis, is then adjusted for percent moisture such that the data can be reported on a dry-weight basis.

4. If the concentrations of any of the certified compounds are within the certified range of the Volatile Organics in Soil/Sediment Samples by GC/MS method, they will be reported. If the concentrations of any of the certified compounds are not detected or below the certified detection limit of the method, they will be reported as "less than" the certified detection limit. If the concentrations of any of the certified compounds exceed the certified range, they should be reported as either "greater than" the upper certified concentration or a smaller sample aliquot (i.e., less than 0.02 mL) should be taken for purge-and-trap analysis.
5. Results will be reported in terms of concentrations in the original matrix and certified analytes will be corrected for recoveries (using the accuracy obtained during method certification).

B. UNDOCUMENTED COMPOUNDS

1. The following calculations are performed to determine the concentrations of compounds which are detected but which have not undergone the method documentation:

$$\text{Concentration (micrograms purged)} = (A_s C_{is}) / (A_{is}) (RF)$$

where: A_s = Area of the characteristic ion for the analyte to be measured,

A_{is} = Area of the characteristic ion for the internal standard,

C_{is} = Micrograms of the internal standard purged,
and

RF = Response factor of the internal standard
(RF=1).

2. Estimates of concentrations of these undocumented compounds will be: (1) reported to only one significant figure, and (2) reported as the concentration in the original matrix assuming 100-percent recovery relative to the closest eluting internal standard.

7. REFERENCES

- U.S. Army Toxic and Hazardous Materials Agency (USATHAMA).
1982. Sampling and Chemical Analysis Quality Assurance
Program for U.S. Army Toxic and Hazardous Materials Agency
(USATHAMA). Aberdeen Proving Ground, Md.
- U.S. Environmental Protection Agency (EPA). 1982. EPA Test
Methods: Methods for Organic Chemical Analysis of Municipal
and Industrial Wastewater. Purgeables--Method 624.
Environmental Monitoring and Support Laboratory, Cincinnati,
Ohio, EPA- 600/4-82/057.

8. DATA

SCANS 1 TO 850

DATA: K305160

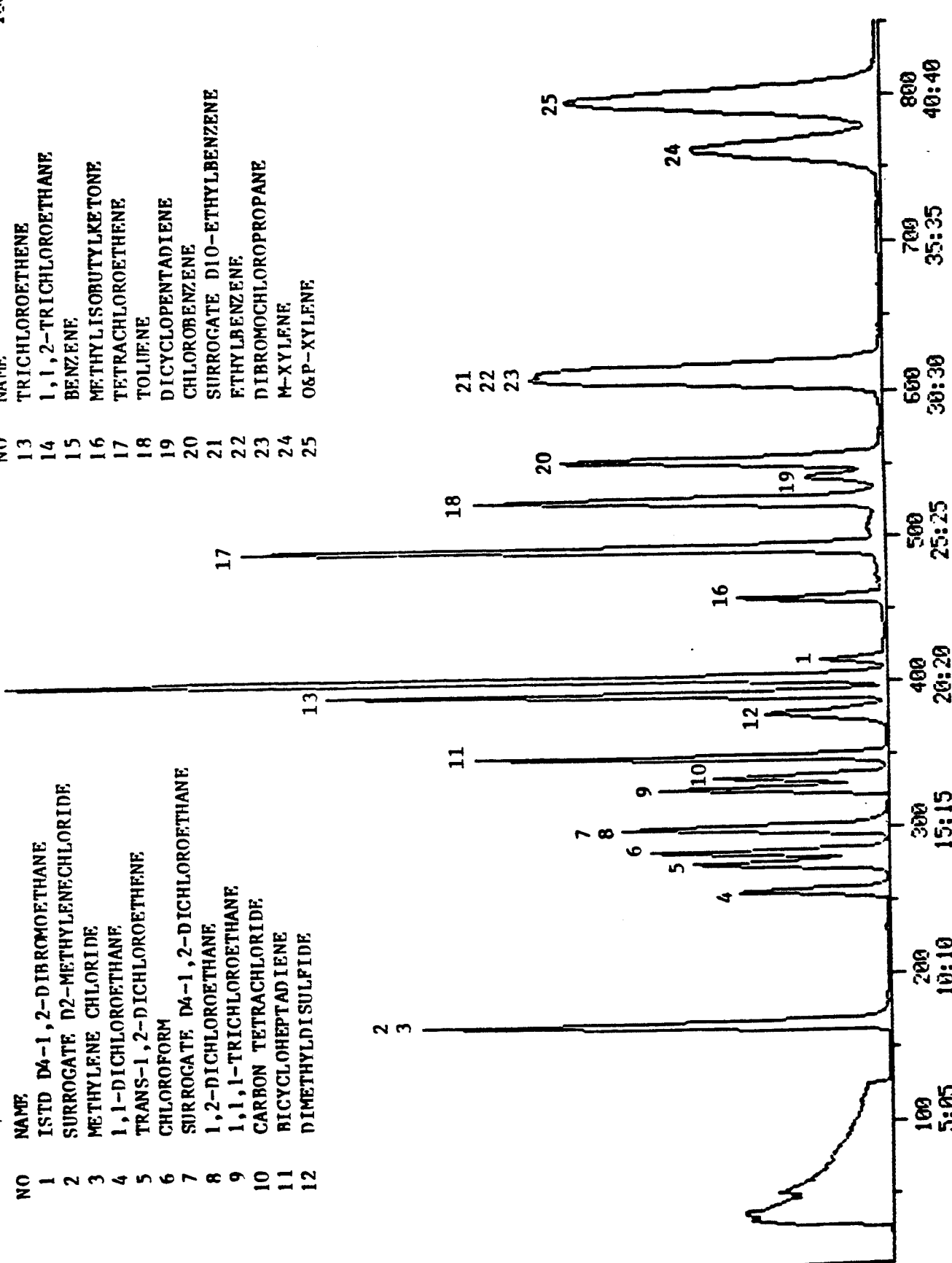
1601530.

RIC
04/05/85 2:02:00
SAMPLE: K305160

NO	NAME	NO	NAME
1	ISTD D4-1,2-DIBROMOETHANE	13	TRICHLOROETHENE
2	SURROGATE D2-METHYLENECHLORIDE	14	1,1,2-TRICHLOROETHANE
3	METHYLENE CHLORIDE	15	BENZENE
4	1,1-DICHLOROETHANE	16	METHYL ISOBUTYLKETONE
5	TRANS-1,2-DICHLOROETHENE	17	TETRACHLOROETHENE
6	CHLOROFORM	18	TOLUENE
7	SURROGATE D4-1,2-DICHLOROETHANE	19	DICYCLOPENTADIENE
8	1,2-DICHLOROETHANE	20	CHLOROBENZENE
9	1,1,1-TRICHLOROETHANE	21	SURROGATE D10-ETHYLBENZENE
10	CARBON TETRACHLORIDE	22	ETHYLBENZENE
11	BICYCLOHEPTADIENE	23	DIBROMOCHLOROPROPANE
12	DIMETHYLDISULFIDE	24	M-XYLENE
		25	O&P-XYLENE

100.0

RIC



SCAN
TIME

UBTL VOLATILES IN SOIL (N-9)

<u>Analyte</u>	<u>Code</u>	<u>Accuracy</u>	<u>Range (ug/g)</u>
Surrogate: D2-Methylene Chloride	CD2CL2	0.847	0.4-25
Methylene Chloride	CH2CL2	0.612	2-25
1,1-Dichloroethane	11DCLE	0.799	2-25
trans-1,2-Dichloroethene	T12DCE	0.807	2-25
Chloroform	CHCL3	1.045	0.3-5
Surrogate: D4-1,2-Dichloroethane	12DCD4	0.752	0.3-25
1,2-Dichloroethane	12DCLE	1.000	0.6-5
1,1,1-Trichloroethane	111TCE	1.044	0.4-10
Carbon Tetrachloride	CCL4	1.077	0.3-10
Bicycloheptadiene	BCHPD	1.000	0.4-10
Dimethyldisulfide	DMDS	0.572	10-25
Trichloroethene	TRCLE	1.150	0.5-25
1,1,2-Trichloroethane	112TCE	1.079	0.4-25
Benzene	C6H6	1.021	0.3-25
Methylisobutyl Ketone	MIBK	1.117	0.7-25
Tetrachloroethene	TCLEE	1.121	0.3-25
Toluene	MEC6H5	0.964	0.3-25
Dicyclopentadiene	DCPD	0.933	0.7-25
Chlorobenzene	CLC6H5	0.926	1-10
Surrogate: D10-Ethylbenzene	ETBD10	0.946	0.3-25
Ethylbenzene	ETC6H5	0.991	0.4-25
Dibromochloropropane	DBCP	1.218	2-25
m-Xylene	13DMB	1.336	0.8-10
o&p-Xylene	XYLEN	0.631	5-50



Test Method

Purgeables — Method 624

1. Scope and Application

1.1 This method covers the determination of a number of purgeable organics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Bromodichloromethane	32101	75-27-4
Bromoform	32104	75-25-2
Bromomethane	34413	74-83-9
Carbon tetrachloride	32102	56-23-5
Chlorobenzene	34301	108-90-7
Chloroethane	34311	75-00-3
2-Chloroethylvinyl ether	34576	110-75-8
Chloroform	32106	67-66-3
Chloromethane	34418	74-87-3
Dibromochloromethane	32105	124-48-1
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
1,1-Dichloroethane	34496	75-34-3
1,2-Dichloroethane	34531	107-06-2
1,1-Dichloroethene	34501	75-35-4
trans-1,2-Dichloroethene	34546	156-60-5
1,2-Dichloropropane	34541	78-87-5
cis-1,3-Dichloropropene	34704	10061-01-5
trans-1,3-Dichloropropene	34699	10061-02-6
Ethyl benzene	34371	100-41-4
Methylene chloride	34423	75-09-2
1,1,2,2-Tetrachloroethane	34516	79-34-5
Tetrachloroethene	34475	127-18-4
Toluene	34010	108-88-3
1,1,1-Trichloroethane	34506	71-55-6
1,1,2-Trichloroethane	34511	79-00-5
Trichloroethene	39180	79-01-6
Trichlorofluoromethane	34488	75-69-4
Vinyl chloride	39175	75-01-4

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET 34215, CAS No. 107-13-1), however, the preferred

method for these two compounds is method 803.

1.3 This is a purge and trap gas chromatographic/mass spectrometer

(GC/MS) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 14.1)(1) for each parameter is listed in Table 1. The MDL for a specific wastewater differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Until the U.S. Environmental Protection Agency establishes performance criteria based upon the results of interlaboratory testing, any alternative GC/MS method which meets the performance criteria described in Section 8.2 will be permitted. Performance must be verified for such modification by analyzing wastewater as described in Section 8.2.2. In addition, the laboratory must successfully participate in the applicable performance evaluation studies.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of purge and trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL sample contained in a specially-designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer(2,3).

3. Interferences

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of

the analysis by running laboratory reagent blanks as described in Section 8.5. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified(5-7) for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon

tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with hole in center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for one hour before use.

5.2 Purge and trap device—The purge and trap device consists of three separate pieces of equipment: the sample purger, trap, and the desorber. Several complete devices are now commercially available.

5.2.1 The sample purger must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15-mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 6.3.1), and 8 cm of silica gel, (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber should be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 220 °C. The desorber design, illustrated in Figure 2, meets these criteria.

5.2.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 GC/MS system.

5.3.1 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

5.3.2 Column—6 ft long \times 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbowax B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

5.3.3 Mass spectrometer—Capable of scanning from 20 to 260 amu every seven seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

5.3.4 GC/MS interface—Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (see Section 10) may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichloro-dimethylsilane.

5.3.5 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.4 Syringes—5-mL glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25-mL, 0.006 inch ID needle.

5.6 Syringe valve—two-way, with Luer ends (three each), if applicable to the purging device.

5.7 Syringe—5-mL, gas-tight with shut-off valve.

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap materials

6.3.1 2,6-Diphenylene oxide polymer—Tenax (60/80 mesh), chromatographic grade or equivalent.

6.3.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.3.3 Silica gel, Davison Chemical, (35/60 mesh), grade-15 or equivalent.

6.4 Methanol—Pesticide quality or equivalent.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the

analyst handles high concentrations of such materials.

6.5.1 Place about 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material as described below:

6.5.2.1 Liquids—Using a 100- μ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

6.5.2.2 Gases—To prepare standards for any of the four halocarbons that boil below 30 °C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol.

6.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 ° to -20 °C and protect from light.

6.5.5 Prepare fresh standards weekly for the four gases and 2-chloroethyl-vinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicate a problem.

6.6 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.1 or 7.4.1 will bracket the

working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards that can be used to determine the accuracy of calibration standards, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 3. Prepare stock standard solutions for each surrogate standard in methanol as described in Section 6.5. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 150 µg/10 mL in water. Store the spiking solution at 4 °C in Teflon sealed glass containers with a minimum of headspace. The solutions should be checked frequently for stability. They should be replaced after six months. The addition of 10 µL of this solution to 5 mL of sample or standard is equivalent to a concentration of 30 µg/L of each surrogate standard. Surrogate standard spiking solutions, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.8 BFB Standard—Prepare a 25 µg/µL solution of BFB in methanol.

7. Calibration

7.1 Assemble a purge and trap device that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by back flushing with an inert gas flow of at least 20 mL/min. Prior to use, daily condition traps 10 minutes while backflushing at 180 °C.

7.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in Table 1. Calibrate the purge and trap-GC/MS system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µL of one or more second-

ary dilution standards to 50, 250, or 500 mL of reagent water. A 25-µL syringe with a 0.006 inch ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL (See Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system. Aqueous standards may be stored up to 24 hours, if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after one hour.

7.3.2 Analyze each calibration standard according to Section 11, and tabulate the area response of the primary characteristic ion (See Table 4) against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.4 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. Due to their generally unique retention times, bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane have been used successfully as internal standards.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal

standards using the procedures described in Sections 6.5 and 6.6. It is recommended that the secondary dilution standard be prepared at a concentration of 15 µg/mL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

7.4.3 Analyze each calibration standard, according to Section 11, adding 10 µL of internal standard spiking solution directly to the syringe (Section 11.4). Tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate response factors (RF) for each compound using equation 1.

$$\text{Eq. 1 } RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Area of the characteristic ion for the parameter to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve or response ratios, A_s/A_{is} , vs. RF.

7.4.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted to certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each parameter to be measured. Using stock standards, prepare a quality control check sample concentrate in methanol 500 times more concentrated than the selected concentrations. Quality control check sample concentrates, appropriate for use with this method, will be available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

8.2.2 Using a syringe, add 10 μ L of the check sample concentrate and 10 μ L of the surrogate standard dosing solution (Section 6.7) to each of a minimum of four 5-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 11.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for all parameters and surrogate standards. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using Table 5, note the average recovery (X) and standard deviation (p) expected for each method parameter. Compare these to the calculated values for R and s. If $s > p$ or $|X - R| > p$, review potential problem areas and repeat the test.

8.2.5 The U.S. Environmental Protection Agency plans to establish performance criteria for R and s based upon the results of interlaboratory testing. When they become available, these criteria must be met before any samples may be analyzed.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.3:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts⁽⁸⁾ that are useful in observing trends in performance. The control limits above must be replaced by method performance criteria as they become available from the U.S. Environmental Protection Agency.

8.3.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly⁽⁸⁾.

8.4 The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Each day, the analyst must demonstrate, through the analysis of reagent water, that interferences from the analytical system are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature

of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site. U.S. Environmental Protection Agency methods 330.4 and 330.5 may be used for measurement of residual chlorine⁽⁹⁾. Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions⁽³⁾. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1 + 1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2. If chlorine residual is present, add sodium thiosulfate to another sample container and fill as in Section 9.2 and mix thoroughly.

9.4 All samples must be analyzed within 14 days of collection.

10. Daily GC/MS Performance Tests

10.1 At the beginning of each day that analyses are to be performed, the

GC/MS system must be checked to see if acceptable performance criteria are achieved for BFB⁽¹⁰⁾. The performance test must be passed before any samples, blanks, or standards are analyzed, unless the instrument has met the DFTPP test described in method 625 earlier in the day⁽¹¹⁾.

10.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 Volts (nominal)
Mass Range: 20 to 260
Scan Time: to give at least 5 scans per peak but not to exceed 7 seconds per scan.

10.3 At the beginning of each day, inject 2 μL of BFB solution directly on column. Alternately, add 2 μL of BFB solution to 5.0 mL of reagent water or standard solution and analyze according to Section 11. Obtain a background corrected mass spectrum of BFB and check that all the key ion criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

11. Sample Extraction and Gas Chromatography

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and method detection limits that were achieved under these conditions. An example of the parameter separations achieved by Column 1 is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

11.2 After achieving the key ion abundance criteria in Section 10, calibrate the system daily as described in Section 7.

11.3 Adjust the purge gas (helium) flow rate to 40 ± 3 mL/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

11.4 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the

sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 μL of the surrogate spiking solution (Section 6.7) and, if applicable, 10.0 μL of the internal standard spiking solution (Section 7.4.2) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution.

11.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

11.6 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

11.7 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for four minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial temperature of 45°C.

11.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

11.9 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 230°C may be employed, however, the higher temperature will shorten the useful life of the trap. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

11.10 If the response for any ion exceeds the working range of the system, dilute the sample aliquot in the second syringe with reagent water and reanalyze.

12. Qualitative Identification

12.1 Obtain EICPs for the primary ion (Table 4) and at least two secondary ions for each parameter of interest. The following criteria must be met to make a qualitative identification.

12.1.1 The characteristic ions of each parameter of interest must maximize in the same or within one scan of each other.

12.1.2 The retention time must fall within ± 30 seconds of the retention time of the authentic compound.

12.1.3 The relative peak heights of the three characteristic ions in the EICPs must fall within $\pm 20\%$ of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

12.2 Structural isomers that have very similar mass spectra and less than 30 seconds difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When a parameter has been identified, the quantitation of that parameter should be based on the integrated abundance from the EICP of the first listed characteristic ion given in Table 4. If the sample produces an interference for the primary ion, use a secondary characteristic ion to quantitate. Quantitation may be performed using the external or internal standard techniques.

13.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the area of the characteristic ion using the calibration curve or calibration factor in Section 7.3.2.

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and equation 2.

Eq. 2.
Concentration $\mu\text{g/L} = (A_s C_{is}) / (A_{is}) (RF)$
where:

- A_s = Area of the characteristic ion for the parameter or surrogate standard to be measured.
 A_{is} = Area of the characteristic ion for the internal standard.
 C_{is} = Concentration of the internal standard.

13.2 Report results in micrograms per liter. The results for cis- and trans-1,3 dichloropropene should be reported as total 1,3-dichloropropene (STORET No. 34561, CAS No. 542-75-6). When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 If any of the surrogate standard recoveries fall outside the control limits which were established as directed in Section 8.4, data for all parameters determined by this method in that sample must be labeled as suspect.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero⁽¹⁾. The MDL concentrations listed in Table 1 were obtained using reagent water⁽¹²⁾. Similar results were achieved using representative wastewaters.

14.2 The average recoveries and the average standard deviations of the percent recoveries, presented in Table 5, were the result of a study of the accuracy and precision of this method by several laboratories. The values listed represent the results from 2 to 4 laboratories⁽¹³⁾.

14.3 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

References

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12. "Method Detection Limit for Methods 624 and 625," Olynyk, P., Budde, W.L. Eichelberger, J.W., unpublished report, October 1980.
13. Kleopfer, R.D., "POTW Toxic Study, Analytical Quality Assurance Final Report," U.S. Environmental Protection Agency, Region VII, Kansas City, Kansas 66115, 1981.

Table 1. Chromatographic Conditions and Method Detection Limits

Parameter	Retention Time (min.) Column 1	Method Detection Limit (µg/L)
Chloromethane	2.3	nd
Bromomethane	3.1	nd
Vinyl chloride	3.8	nd
Chloroethane	4.6	nd
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	nd
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	nd
2-Chloroethylvinyl ether	18.6	nd
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	nd
1,2-Dichlorobenzene	35.0	nd
1,4-Dichlorobenzene	35.4	nd

nd = not determined

Column conditions: Carboxpak B (60/80 mesh) coated with 1% SP-1000 packed in a 6 ft by 2 mm ID glass column with helium carrier gas at a flow rate of 30 mL/min. Column temperature is isothermal at 45°C for 3 min, then programmed at 8°C per minute to 220°C and held for 15 min.

Table 2. BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but < 101% of mass 174
177	5 to 9% of mass 176

Table 3. Suggested Surrogate and Internal Standards

Compound	Retention Time (min.) ^a	Primary Ion	Secondary Ions
Surrogate Standards			
Benzene d-6	17.0	84	—
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane d-4	12.1	102	—
1,4-Difluorobenzene	19.6	114	63, 88
Ethylbenzene d-5	26.4	111	—
Ethylbenzene d-10	26.4	98	—
Fluorobenzene	18.4	96	70
Pentafluorobenzene	23.5	168	—
Internal Standards			
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	19.2	77	79, 156
1,4-Dichlorobutane	25.8	55	90, 92

^aFor chromatographic conditions, see Table 1.

Table 4. Characteristic Ions for Purgeable Organics

Parameter	Primary Ion	Secondary Ions
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
trans-1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	98	62, 64, 100
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Bromodichloromethane	127	83, 85, 129
1,2-Dichloropropane	112	63, 65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Benzene	78	
Dibromochloromethane	127	129, 208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
cis-1,3-Dichloropropene	75	77
2-Chloroethylvinyl ether	106	63, 65
Bromoform	173	171, 175, 250, 252, 254, 256
1,1,2,2-Tetrachloroethane	168	83, 85, 131, 133, 166
Tetrachloroethene	164	129, 131, 166
Toluene	52	91
Chlorobenzene	112	114
Ethyl benzene	106	91
1,3-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113

Table 5. Accuracy and Precision for Purgeable Organics

Parameter	Reagent Water		Wastewater	
	Average Percent Recovery	Standard Deviation (%)	Average Percent Recovery	Standard Deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethylvinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/L.

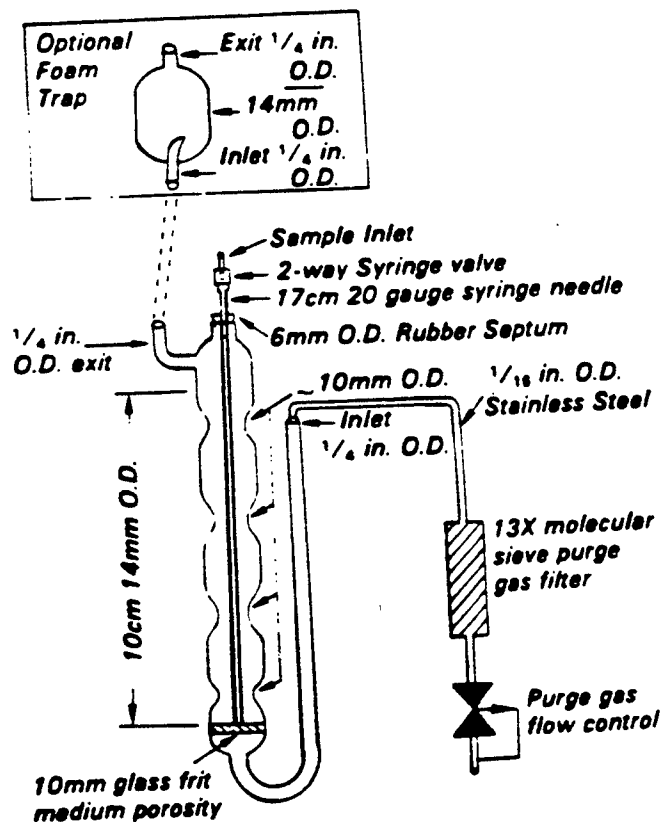


Figure 1. Purging device

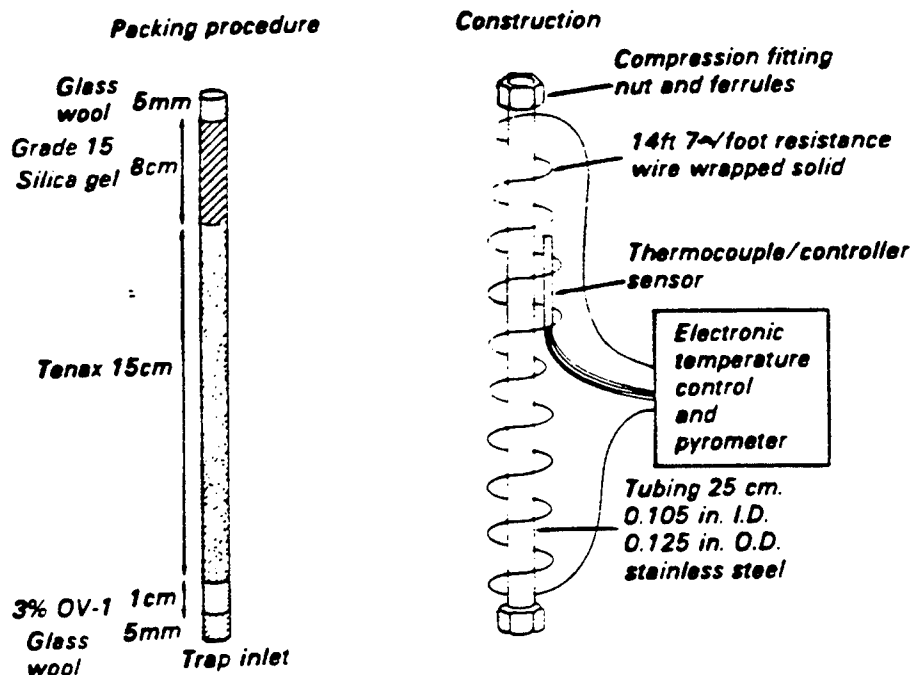


Figure 2. Trap packings and construction to include desorb capability

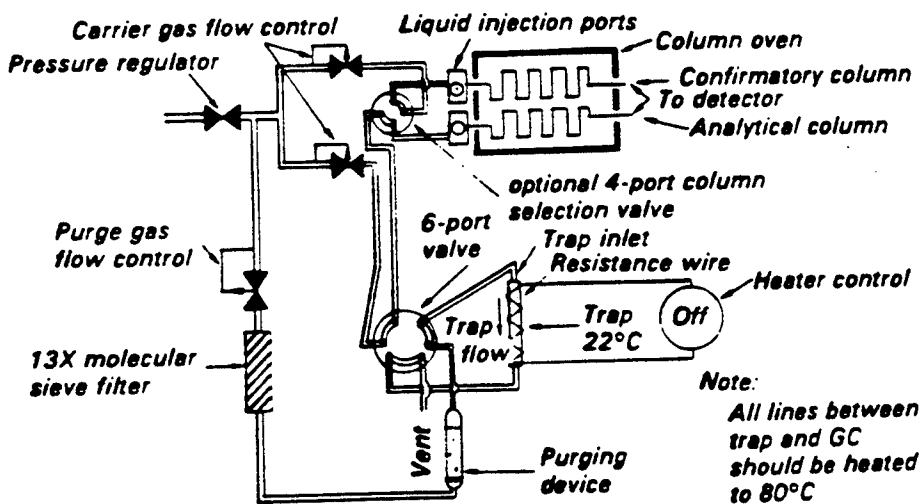


Figure 3. Schematic of purge and trap device — purge mode

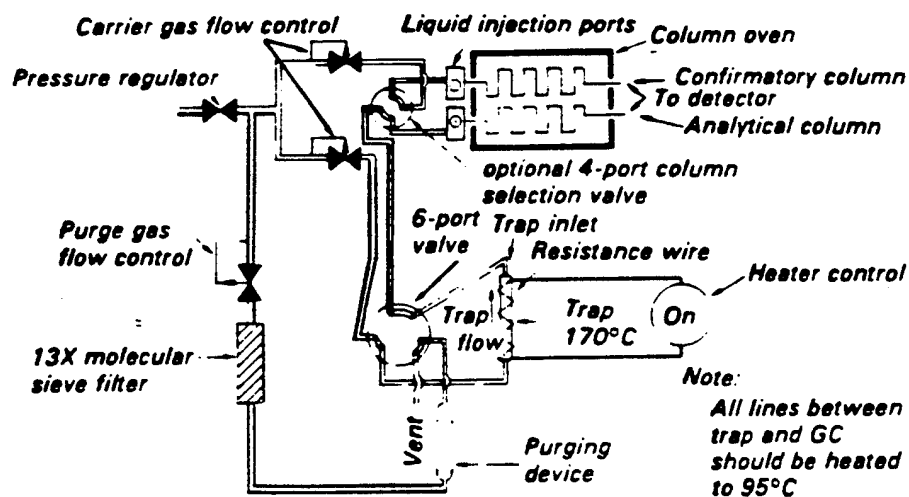


Figure 4. Schematic of purge and trap device — desorb mode

Column: 1% SP-1000 on Supelcoport
 Program: 45°C. 3 min., 8° per min. to 220°C.
 Detector: Mass spectrometer

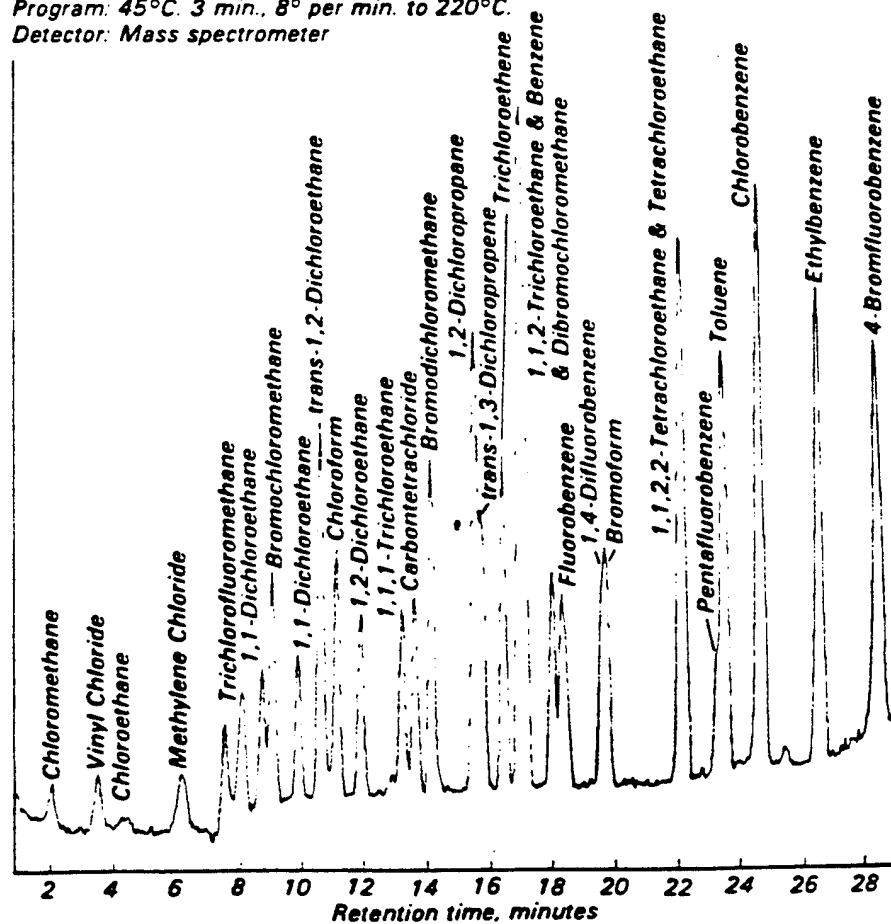


Figure 5. Gas chromatogram of volatile organics by purge and trap.

USATHAMA CERTIFIED METHOD K9 FOR CAL

USATHAMA CERTIFIED METHOD #K9

Identification and Determination of Selected Volatile Organics in Soil and Solids

(CAL Version 4, 5/15/85)
(USATHAMA Version 1, 5/6/85)

- I. Application: The method is designed as a semi-quantitative method for selected volatile organic compounds in soil and solid samples based on solvent extraction and purge/trap GC/MS determination (methanol extraction and EPA Method 8240). The method is certified as semiquantitative based on a standard reference soil.

A. Tested Concentration Ranges:
0.25 to 25 ug/g (see I-C, below).

B. Sensitivity:

Analyte	RRT	Fragment Ion	Sensitivity	
			Ion Peak Area	conc. (ug/g)
ETC6H5	1.469	106	10539	0.3
C6H6	0.946	78	26812	0.3
MIBK	1.121	58	3214	0.3
DMDS	0.889	94	10009	0.8
11DCLE	0.585	63	11670	0.9
12DCLE	0.690	62	6853	0.3
111TCE	0.760	97	7595	0.3
112TCE	0.962	97	8176	0.3
CH2CL2	0.375	84	16387	0.7
CHCL3	0.652	83	11517	0.3
CCL4	0.779	117	5640	0.3
T12DCE	0.620	96	6139	0.3
MEC6H5	1.288	92	23038	0.3
CLC6H5	1.350	112	20921	0.3
TCLEE	1.218	164	6153	0.3
TRCLE	0.919	130	7593	0.3
13DMB	1.736	91	23232	0.7
XYLEN	1.798	91	44727	0.3
DBCP	1.496	157	1133	0.4
DCPD	1.345	66	16038	0.3
BCHPD	0.822	91	22017	0.3
12DCD4	0.685	67	4077	0.3
CD2CL2	0.372	53	2431	0.3
ETBD10	1.456	98	35039	0.3
1,2-Dibromoethane-d4(I.S.)	1.000	111	---	---

RRT = Retention time relative to 1,2-dibromoethane-d4
internal standard (retention time = 19.0 minutes).

C. Certified Detection Limits, Ranges and Accuracy:

<u>Analyte</u>	<u>Detection Limit (ug/g)</u>	<u>Upper Concentration Range (ug/g)</u>	<u>Accuracy</u>
ETC6H5	0.3	25	0.920
C6H6	0.3	25	0.922
MIBK	0.3	25	0.997
DMS	0.8	25	1.12
11DCLE	0.9	10	0.972
12DCLE	0.3	25	0.845
111TCE	0.3	10	1.00
112TCE	0.3	25	0.923
CH2CL2	0.7	25	0.790
CHCL3	0.3	10	0.969
CCL4	0.3	25	0.887
T12DCE	0.3	25	0.921
MEC6H5	0.3	25	0.879
CLC6H5	0.3	25	0.883
TCLEE	0.3	25	0.847
TRCLE	0.3	25	0.883
13DMB	0.7	25	0.917
XYLEN	0.3	25	0.996
DBCP	0.4	25	0.928
DCPD	0.3	25	0.959
BCHPD	0.3	25	0.921
12DCD4	0.3	25	0.842
CD2CL2	0.3	25	1.03
ETBD10	0.3	25	0.919

D. Interferences: Coeluters with similar ions could interfere.

E. Analysis Rate: One sample extractor and one GC/MS operator can analyze eight samples in an eight hour day.

II. Chemistry:

A. Alternate Nomenclature and Chemical Abstracts Registry Number:

<u>Analyte</u>	<u>CAS Registry Number</u>
ETC6H5 (Ethylbenzene)	100-41-4
C6H5 (Benzene)	71-43-2
MIBK (Methyl isobutyl ketone)	108-10-1
DMDS (Dimethyl disulfide)	624-92-0
11DCLE (1,1-Dichloroethane)	75-35-4
12DCLE (1,2-Dichloroethane)	107-06-2
111TCE (1,1,1-Trichloroethane)	71-55-6
112TCE (1,1,2-Trichloroethane)	79-00-5
CH2CL2 (Methylene chloride)	75-09-2
CHCL3 (Chloroform)	67-66-3
CCL4 (Carbon tetrachloride)	56-23-5
T12DCE (trans-1,2-Dichloroethene)	156-60-5
MEC6H5 (Toluene)	108-88-3
CLC6H5 (Chlorobenzene)	108-90-7
TCLEE (Tetrachloroethene)	127-18-4
TRCLE (Trichloroethene)	79-01-6
13DMB (o-Xylene)	95-47-6
XYLEN (m-Xylene)	108-38-3
XYLEN (p-Xylene)	25493-13-4
DBCP (1,2-Dibromo-3-chloropropane)	96-12-8
DCPD (Dicyclopentadiene)	77-73-6
BCHPD (Bicycloheptadiene)	121-46-0

B. Chemical Reactions: N/A

III. Apparatus:

A. Instrumentation: Finnigan Model 1020 (or equivalent) gas chromatograph-mass spectrometer equipped with a Tekmar Model LSC-2 (or equivalent) purge/trap device. The GC/MS is coupled to an INCOS (or equivalent) computer. The GC/MS/DS system is operated and tuned as described in EPA Method 8240.

B. Parameters:

1. Column: 6 foot by 2 mm (id) glass column packed with 1% SP-1000 on 60/80 mesh Carboxpack B held isothermal at 45°C for 3 min. and temperature programmed at 8°C/min. to 220°C (hold for 10 min.).

2. Conditions: Injector port: 225°C; transfer line: 175°C; carrier gas (helium) at about 20 mL/min.
3. Purge Volume: 20 uL of standards or sample extracts plus 5 uL of internal standard are diluted to 5.0 mL with water and the mixture purged.
4. Retention Times: See I-B above.

C. Hardware/Glassware:

1. 40 mL glass vials with teflon-lined screw caps. The vials are cleaned with methanol and baked at 105°C overnight before use.
2. Volumetric flasks and pipettes as necessary.
3. Platform shaker.
4. Microliter syringes.

D. Chemicals:

1. Methanol: EM "Omnisolve" Quality or equivalent. The methanol is used as received. Each bottle is tested by this method before use in sample extraction.
2. Analytical Reference Standards of Analytes, Surrogates and Internal Standard: BCHD is from Aldrich; 1,2-dibromoethane-d4 is from Cambridge Isotope Labs; 1,1,2-trichloroethane is from Supelco; 1,2-dichloroethane-d4 is from MSD Isotopes; all others are USATHAMA SARMS or interm SARMS.
3. 4-Bromofluorobenzene (BFB).
4. Water: Deionized and distilled water is boiled for 10 minutes and purged with nitrogen for at least 4 hours before use. The water is then maintained under a constant nitrogen purge.

IV. Standards:

- A. Stock Solutions: Individual stock solutions of analytes, surrogates and the internal standard are prepared in methanol in 10 mL volumetric flasks. All chemicals except DCPD (which is weighed) are liquids and are therefore prepared by volume measurements using microliter syringes.

Chemical	Density (g/mL)	Volume Pipetted (uL)	ug/mL conc.
Ethylbenzene	0.867	115	10,000
Benzene	0.874	114	10,000
MIBK	0.800	125	10,000
DMDS	1.05	95.2	10,000
1,1-Dichloroethane	1.18	84.7	10,000
1,2-Dichloroethane	1.26	79.4	10,000
1,1,1-Trichloroethane	1.34	74.6	10,000
1,1,2-Trichloroethane	1.44	69.4	10,000
Methylene chloride	1.33	75.2	10,000
Chloroform	1.49	67.1	10,000
Carbon tetrachloride	1.59	62.9	10,000
trans-1,2-Dichloroethene	1.26	79.4	10,000
Toluene	0.867	115	10,000
Chlorobenzene	1.11	90.1	10,000
Tetrachloroethene	1.62	61.7	10,000
Trichloroethene	1.46	68.5	10,000
o-Xylene	0.897	111	10,000
m-Xylene	0.868	115	10,000
p-Xylene	0.866	115	10,000
DBCP	2.09	47.8	10,000
Dicyclopentadiene	(solid)	(100 mg)	10,000
Bicycloheptadiene	0.854	117	10,000
Methylene chloride-d4	1.36	73.5	10,000
1,2-Dichloroethane-d4	1.26	79.4	10,000
Ethyl benzene-d10	0.87	115	10,000
1,2-Dibromoethane-d4	2.18	45.9	10,000

- B. GC/MS Internal Standard: The stock solution of 1,2-dibromoethane-d4 is diluted in methanol to give a 50 ug/mL working standard. The internal standard working solution is always added at 5.0 uL to the 5.0 mL water solutions of standards or sample extracts just prior to introduction into the purge unit.

- C. Surrogate Spike Standards: The stock solutions of the three deuterated surrogates (methylene chloride-d4, 1,2-dichloroethane-d4, ethyl benzene-d10) are combined and diluted in methanol to give the following:

Code	Preparation	Surrogate Conc. (ug/mL)
624-SUR-G	2.50 mL each stock to 100 mL	250
624-SUR-F2	40.0 mL 624-SUR-G to 100 mL	100
624-SUR-F	10.0 mL 624-SUR-G to 50 mL	50
624-SUR-E	5.0 mL 624-SUR-G to 50 mL	25
624-SUR-D	2.0 mL 624-SUR-G to 50 mL	10
624-SUR-C	1.0 mL 624-SUR-G to 50 mL	5.0
624-SUR-B	0.50 mL 624-SUR-G to 50 mL	2.5

Solutions are stored in 100 mL amber glass bottles at 4°C.

- D. Analyte Spike Standards: The stock solutions of the twenty-two analytes are combined and diluted in methanol to give the following:

Code	Preparation	Analyte Conc. (ug/mL)
624-SS-G	2.50 mL each stock to 100 mL	250
624-SS-F2	20.0 mL 624-SS-G to 50 mL	100
624-SS-F	10 mL 624-SS-G to 50 mL	50
624-SS-E	5.0 mL 624-SS-G to 50 mL	25
624-SS-D	2.0 mL 624-SS-G to 50 mL	10
624-SS-C	1.0 mL 624-SS-G to 50 mL	5.0
624-SS-B	0.50 mL 624-SS-G to 50 mL	2.5

Solutions are stored in 100 mL amber glass bottles at 4°C.

- E. GC/MS Working Standards: The surrogate spike standard mixes and analyte spike standard mixes prepared in IV-C and IV-D above are combined and diluted in methanol as follows:

Code	Preparation	Surrogate and Analyte Conc. (ug/mL)
624-WS-G	1.0 mL ea SS-G & SUR-G to 10 mL	25
624-WS-F2	1.0 mL ea SS-F2 & SUR-F2 to 10 mL	10
624-WS-F	1.0 mL ea SS-F & SUR-F to 10 mL	5.0
624-WS-E	1.0 mL ea SS-E & SUR-E to 10 mL	2.5
624-WS-D	1.0 mL ea SS-D & SUR-D to 10 mL	1.0
624-WS-C	1.0 mL ea SS-C & SUR-C to 10 mL	0.50
624-WS-B	1.0 mL ea SS-B & SUR-B to 10 mL	0.25

Solutions are stored in 15 mL test tubes at 4°C.

V. Procedures:

- A. Analysis of Certification Control Spikes Only: The GC/MS system was calibrated by purging 20 uL aliquots of each GC/MS Working Standard plus 5.0 uL of Internal Standard in 5.0 mL of water. The standard curve was linear (correlation coefficient >0.996) throughout the standard range (1.0 ug/L through 100 ug/L in the 5.0 mL purge sample).

Certification control spikes were then prepared using 10g of standard soil as indicated in Table I (attached). In all cases, 20 uL of the methanol extracts were combined with 5.0 uL of Internal Standard solution in 5.0 mL of water. Results of the Hubaux-Vos certification charts are attached.

B. Analysis of Environmental Standards:

1. GC/MS Calibration: Response factors (RFs) and a standard curve for each analyte and each surrogate are developed via the 1,2-dibromoethane-d4 internal standard by purging 20 uL aliquots of the GC/MS Working Standards (624-WS-G, -F2, -E & -C), diluted to 5.0 mL with water plus 5.0 uL of the 50 ug/mL internal standard working solution. This provides a four-point standard curve from 2.0 ug/L to 100 ug/L in the purge water, equivalent to 0.50 ug/g to 25 ug/g of original solid sample. The response factors are updated daily, before the analysis of sample extracts, using the 10 ug/mL standard mix (624-WS-F2). If the daily calibration RFs differ (using "%D" as defined below) from the average RFs by more than 25% for any of the surrogates, then a new standard curve and a new set of response factors must be made. If the daily calibration is within the acceptable "%D" window, then analysis of the sample extracts can proceed.

The percent difference (%D) calculation is $[(\text{daily RF} - \text{average RF}) / \text{average RF}] \times 100$. Calculation and tabulation of daily RFs, average RF's and "%D" are easily done with INCOS or equivalent software.

The GC/MS system is tuned to meet EPA criteria for BFB daily, as described in EPA Method 8240 (attached).

2. Extraction: Subsamples (10g + 0.1g) will usually be received in 40 mL amber glass vials with teflon-lined screw caps with 9.0 mL of methanol already added. If subsamples are prepared in the lab, 10g (+ 0.1g) portions will be placed in the vials along with 9.0 mL of methanol. In either case, a 1.0 mL aliquot of surrogate standard 624-SUR-F2 is added to samples and the sample set "method blank" (10g of standard soil) prior to extraction. This surrogate spike provides each of the surrogates at 10 ug/g in every sample. After addition of the surrogates, the samples are extracted by shaking for four hours. After allowing the solids to settle, the methanol extracts are analyzed as below.
3. GC/MS Analysis: A 20 uL sample extract aliquot (equivalent to 0.020 g sample) is combined with 5.0 uL of 50 ug/mL internal standard working solution and 5.0 mL of water in a 5 mL gas-tight syringe. The mixture is introduced into the purge chamber and processed as described in EPA Method 8240.
4. Unknown GC/MS Peaks: Unknown GC/MS peaks will be tentatively identified by computer assisted comparison to the NBS 31,000 entry mass spectral library (or equivalent). The mass spectroscopist will use the INCOS (or equivalent) "fit", "purity" and "refit" criteria to assign probabilities of correct structural assignment. Hardcopy mass spectra of all unknowns will be provided with the report.

The five largest unknown peaks which are present in excess of ten percent of the area of the m/e 111 peak for 1,2-dibromoethane-d4 internal standard will be library searched.

VI. Calculations:

$$A. \text{ ug analyte/mL extract} = \frac{(\text{area of analyte peak}) (50 \text{ ug/mL I.S.})}{(\text{area of I.S.}) (\text{analyte RF})}$$

Where I.S.=1,2-dibromoethane-d4 internal standard

$$RF = \text{Response factor} = \frac{(\text{area of analyte peak}) (50 \text{ ug/mL I.S.})}{(\text{area of I.S.}) (\text{conc. of analyte})}$$

$$B. \text{ ug analyte/g sample} = \text{ppm} = \frac{\text{ug analyte/mL extract}}{\text{g sample/mL extract}}$$

C. Final results are reported on a dry-weight basis and are corrected for percent recovery (based on certification data).

VII. References: A copy of EPA Method 8240 (Test Methods for Evaluating Solid Wastes, US EPA SW-846, 2nd Edition, July 1982) is attached.

Table I
Certification Control Spike Analysis

Sample ID	volume of analyte std added	volume of surrogate std added	volume of methanol added	ug/g analytes & surrogates added	ug/L in 5.0 mL purge water
Blank	0.0	0.0	10.0 mL	0.0	0.0
0.5X	1.0 mL 624-SS-B	1.0 mL 624-SUR-B	8.0 mL	0.25	1.0
1X	1.0 mL 624-SS-C	1.0 mL 624-SUR-C	8.0 mL	0.50	2.0
2X	1.0 mL 624-SS-D	1.0 mL 624-SUR-D	8.0 mL	1.0	4.0
5X	1.0 mL 624-SS-E	1.0 mL 624-SUR-E	8.0 mL	2.5	10
10X	1.0 mL 624-SS-F	1.0 mL 624-SUR-F	8.0 mL	5.0	20
20X	2.0 mL 624-SS-F	2.0 mL 624-SUR-F	6.0 mL	10	40
50X	1.0 mL 624-SS-G	1.0 mL 624-SUR-G	8.0 mL	25	100

RIC

05/10/85 9:34:00

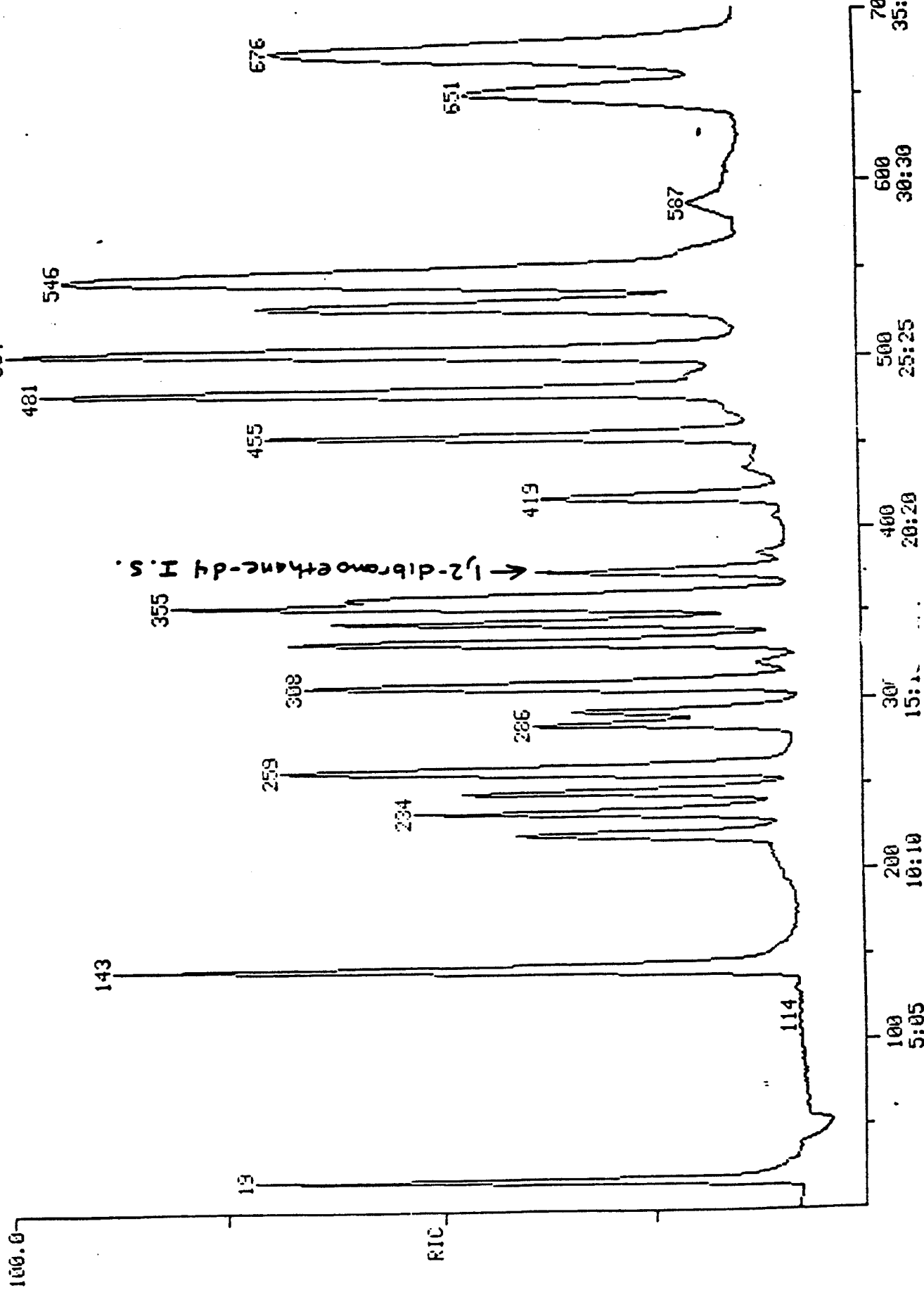
SAMPLE: RM UOA STANDARD 10UG/ML 20UL IN 5ML

RANGE: C 1, 700 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

DATA: ST9850510 #1
CALL: FC439 #12

SCANS 1 TO 700

292352



METHOD 8240

GC/MS METHOD FOR VOLATILE ORGANICS

1.0 Scope and Application

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 The detection limit of Method 8240 for an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples containing more than 1 mg/g of total volatile material, the detection limit is proportionately higher.

1.3 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 Summary of Method

2.1 The volatile compounds are introduced to the gas chromatograph by direct injection, the Headspace Method (Method 5020), or the Purge-and-Trap Method (Method 5030). Method 5030 should be used for groundwater analysis. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample can be dispersed in methanol or polyethylene glycol (PEG) to dissolve the volatile organic constituents. A portion of the methanolic or PEG solution is combined with water in a specially designed purging chamber. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

2.3 An aliquot of each sample must be spiked with an appropriate standard to determine percent recovery and detection limits for that sample.

2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1 ^a	Method detection limit (µg/l)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

^aColumn conditions: Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

3.0 Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the particular waste or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences under the conditions of the analysis by running method blanks. Method blanks are run by analyzing organic-free water in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce cross contamination, the purging device and sample syringe should be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.2.

4.0 Apparatus and Materials

4.1 Sampling equipment

4.1.1 Vial: 25-ml capacity or larger, equipped with a screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for 1 hr at 105° C before use.

4.1.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105° C for 1 hr before use.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

4.2.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

4.3 Gas chromatograph/mass spectrometer system

4.3.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carbowack B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

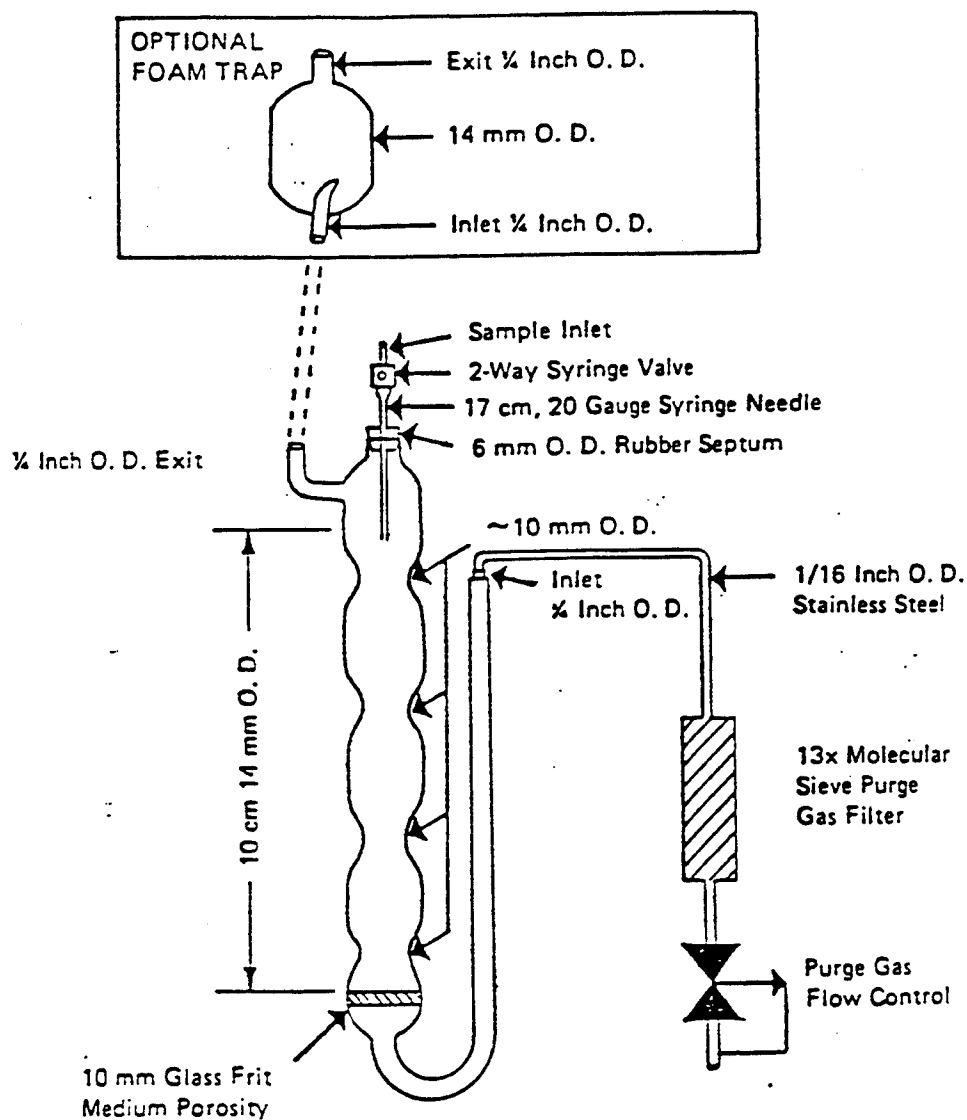


Figure 1. Purging chamber.

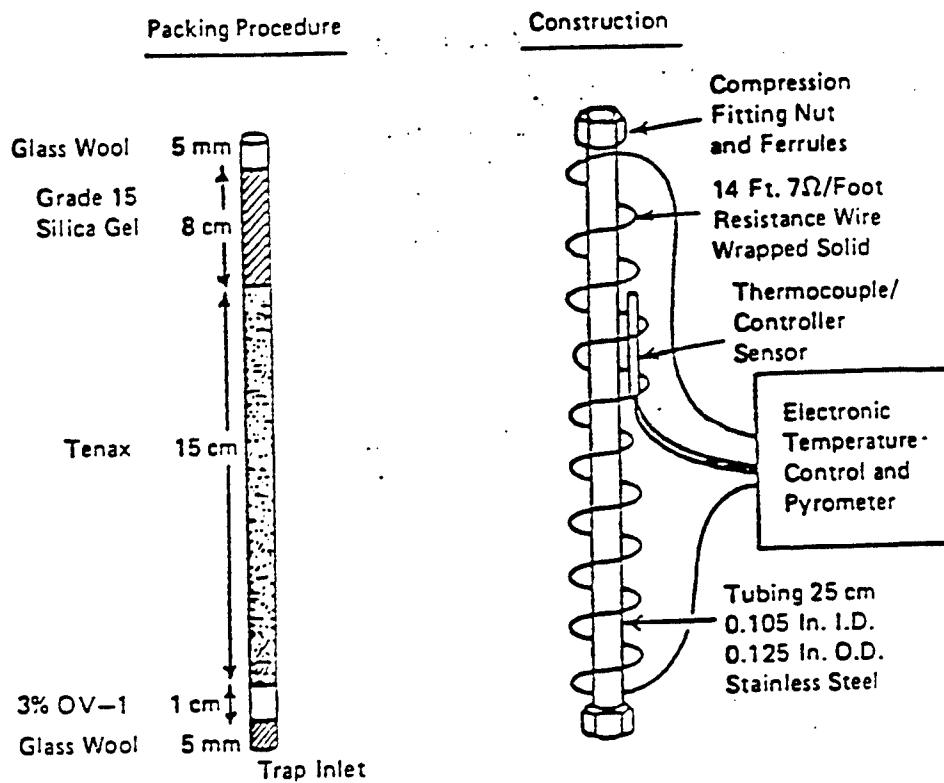


Figure 2. Trap packings and construction to include desorb capability.

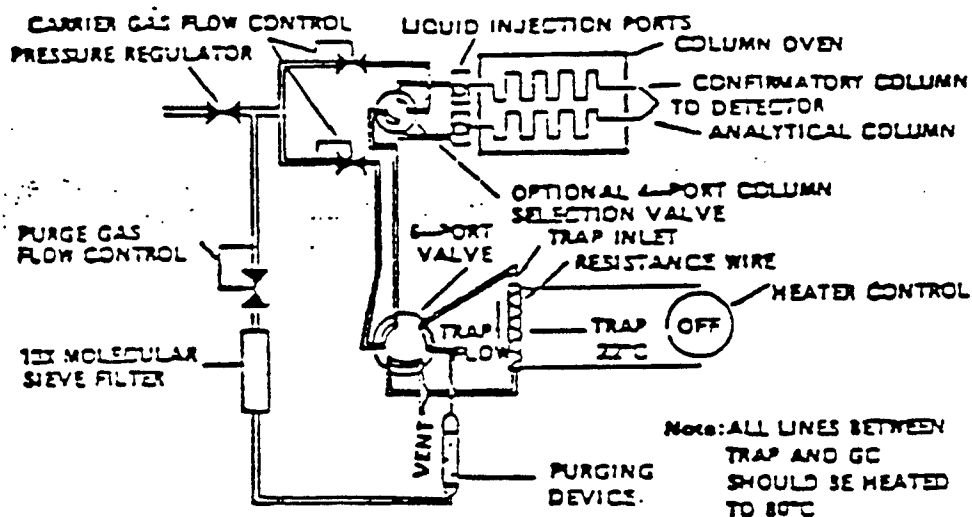


FIGURE 3. Schematic of purge and trap device - purge mode

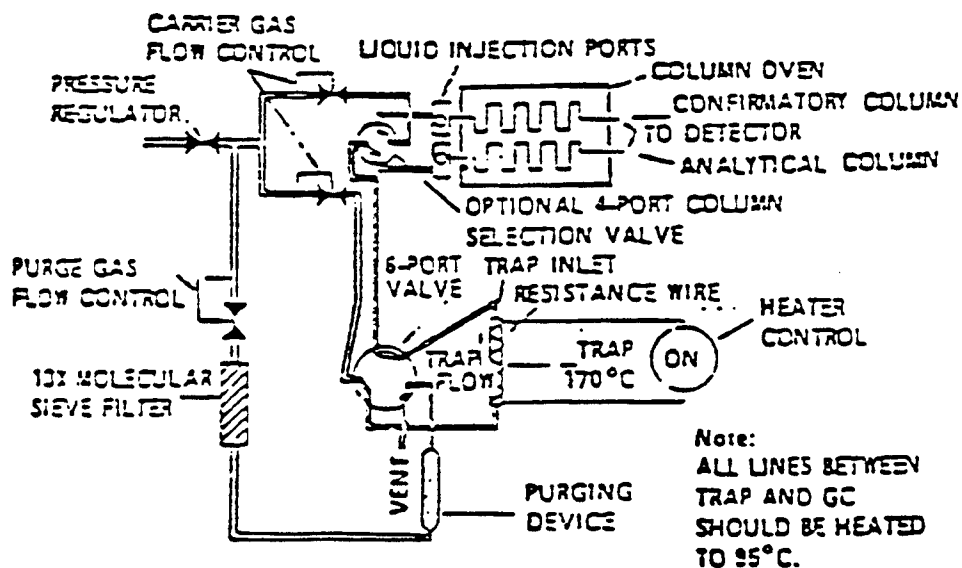


Figure 4. Schematic of purge and trap device - desorb mode

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Hardware and software must be available to transform the data into a compatible format. These generally consist of a 9-inch, 800-bpi tape drive and the associated software.

4.4 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Samples should be introduced into the syringe by (1) removing the plunger from the syringe, (2) pouring the sample into the barrel, and (3) replacing the barrel and inverting the syringe to remove any air trapped in the syringe. Do not draw the sample up into the syringe. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syringe.

TABLE 2. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 100% of mass 174
177	5 to 9% of mass 176

4.5 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.6 Micro syringes: 10- μ l, 25- μ l, 100- μ l, 250- μ l, and 1000- μ l. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.7 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation.

4.8 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.9 Syringe valve: 2-way, with Luer ends (2 each) (Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting, or equivalent).

4.10 Syringe: 5-ml, gas-tight with shut-off valve.

4.11 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.12 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.13 Rotary evaporator: equipped with Teflon-coated seals (Buchi Rotavapor R-110, or equivalent).

4.14 Vacuum pump: mechanical, two-stage.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn by analysts when handling high concentrations of these materials.

5.5.1 Place about 9.8 ml of methanol in a 10-ml ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material as described below.

5.5.2.1 Liquids: Using a 100- μ l syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30° C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-ml valved gas-tight syringe with a reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol.

5.5.3 Reweigh, dilute to volume, stopper, then mix by gently inverting the flask several times. Calculate the concentration in μ g/ μ l per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20° C and protect from light.

5.5.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards; secondary dilution solutions: Using stock solutions described in Section 5.5, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the methanol or aqueous PEG calibration solutions prepared as described in Section 6.3.2 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards from them.

5.7 Surrogate standards: Surrogate standards may be added to samples and calibration solutions to assess the effect of the sample matrix on recovery efficiency. The compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride. Prepare methanolic solutions of the surrogate standards using the procedures described in Sections 5.5 and 5.6. The

concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D₄-1,2-dichloroethane, D₆-benzene, and D₅-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

7.0 Procedure

7.1 Calibration

7.1.1 Assemble a purge-and-trap device that meets the specifications in Section 4.2 and connect the device to a GC/MS system. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, condition the trap daily for 10 min while backflushing at 180° C.

7.1.2 Operate the gas chromatograph using the conditions described in Section 7.3.5 and operate the mass spectrometer using the conditions described in Section 7.3.2.

7.1.3 Calibration procedure

7.1.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be at a concentration near but above the method detection limit. The remaining two concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3.2 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. To the purging device, add 5.0 ml of reagent water or reagent water/PEG solution. This solution is prepared by taking 4.0 ml of reagent water or reagent PEG and diluting to 100 ml with reagent water. The reagent water/PEG solution is added to the purging device using a 5-ml glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of a 20-gauge needle. Next, using a 10- μ l or 25- μ l micro-syringe equipped with a long needle (see Section 4.6), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 5.6). Add the aliquot of calibration solution directly to the reagent water or reagent water/PEG solution in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe be sure that the end of the syringe needle is well beneath the surface of the reagent water or water/PEG solution. Similarly, add 20 μ l of the internal standard solution (see Section 5.10). Close the 2-way syringe valve at the sample inlet.

7.1.3.3 Carry out the purge and analysis procedure as described in Section 7.3.4. Tabulate the area response of the primary characteristic ion against concentration for each compound

including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_S = Area of the primary characteristic ion for the compound to be measured

A_{IS} = Area of the primary characteristic ion of the internal standard

C_{IS} = Concentration of the internal standard

C_S = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{IS} , versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy: 70 volts (nominal)

Mass Range: 40 to 250 amu

Scan Time: to give approximately 6 scans per peak but not to exceed 3 sec per scan.

7.2.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1. A solution containing 20 ng of BFB may be injected onto the gas chromatographic column in order to check the key ion criteria.

7.2.4 The peak intensity of D₆-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D₆-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D₆-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D₆-benzene observed during calibration was 355,000 area counts, then each subsequent sample or blank must give a D₆-benzene peak intensity of between 250,000 and 500,000 area counts. If the D₆-benzene peak intensity is outside the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

7.3 Sample extraction and analysis

7.3.1 The analytical procedure involves extracting the non-aqueous sample with methanol or polyethylene glycol (PEG) and analyzing a portion of the extract by a purge-and-trap GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated total volatile content (TVC) of the sample. The TVC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract by gas chromatography.

7.3.2 The estimated TVC is based on the total area response relative to that of n-nonane for all components eluting prior to the retention time of n-dodecane. The response factor for n-nonane and the retention time of n-dodecane are determined by analyzing a 2- μ l aliquot of an n-hexadecane solution containing 0.20 mg/ml of n-nonane and n-dodecane.

7.3.2.1 The GC analyses are conducted using a flame ionization detector and a 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100-200 mesh Chromosorb W-HP. The column temperature is programmed from 80° C to 280° C at 8°/min and held at 280° for 10 min.

7.3.2.2 Determine the area response for n-nonane and divide by 0.2 to obtain the area response factor. Record the retention time of n-dodecane.

7.3.2.3 Add 1.0 g of sample to 20 ml of n-hexadecane and 2 ml of 2.0 M Na₂HPO₄ contained in a 50-ml glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse

during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2- μ l aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$\text{TVC} = \frac{\text{TAR}_{\text{sample}} - \text{TAR}_{\text{blank}}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR_{sample} = total area response obtained for the sample

TAR_{blank} = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.3.3.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20°C , and protect from light.

7.3.4 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is connected to the purge-and-trap device and that has been flushed with helium during a 7-min trap reconditioning step (see Section 7.3.4.4). The additions are made using an appropriately sized syringe equipped with a 15-cm 20-gauge needle. Open the syringe valve of the sample inlet (shown in Figure 1) and insert the needle through the valve.

7.3.4.1 Add 5.0 ml of reagent water or aqueous sample to which 20.0 μl of the internal standard solution has been added (see Section 5.10) to the purging chamber. Insert the needle of the syringe well below the surface of the water for the addition of the internal standard solution. If the sample is aqueous go to Section 7.3.5.

7.3.4.2 Add an aliquot of the sample extract from Section 7.3.3.4. The total quantity of volatile components injected should not exceed approximately 10 μg . If the total volatile content (TVC) of the sample as determined in Section 7.3.1.4 is 1.0 mg/g or less, use a 200- μl aliquot of the sample extract. If the TVC is greater than 1.0 mg/g, use an aliquot of the sample extract that contains approximately 10 μg of total volatile components; the volume (in μl) of the aliquot to be taken can be calculated by dividing 200 by the TVC. If the TVC is greater than 20 mg/g, take a 500- μl aliquot of the sample extract and dilute to 10 ml with PEG. In this case calculate the aliquot volume (in μl) of the undiluted extract to be taken by dividing 4,000 by the TVC. If the TVC is less than 1.0 mg/g and greater sensitivity is desired, use a large purging chamber containing 25 ml of reagent water and use a 1.0-ml aliquot of the sample extract.

7.3.4.3 Close the 2-way syringe valve at the sample inlet.

7.3.5 The sample in the purging chamber is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

7.3.5.1 Adjust the gas (helium) flow rate to 40 ± 3 ml/min. Set the purging device to purge, and purge the sample for 11.0 ± 0.1 min at ambient temperature.

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

7.4.1.2 The retention time must fall within +30 sec of the retention time of the authentic compound.

7.4.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within +20% of the relative intensities of these ions in a reference mass spectrum. Reference spectra may be generated from the standards analyzed by the analyst or from a reference library. All reference spectra generated from standards must be obtained from an appropriately tuned mass spectrometer.

7.5 Quantitative determination

7.5.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used. Generally, the base peak of the mass spectrum is used.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of the data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1.3 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methanol at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the PEG used for the extraction. Analyze the spiked aliquots according to the method in Section 7.3.

8.2.4 Calculate the average percent recovery, R , and the standard deviation of the percent recovery, s , for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, $s/R \times 100$, must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100% recovery of the surrogate standards. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be

qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Four surrogate standards, namely 1,2-dibromodifluoroethane, bis(perfluoro-isopropyl) ether, fluorobenzene, and m-bromobenzotrifluoride, are recommended for general use to monitor recovery of volatile compounds varying in volatility and polarity.

8.5 Each day, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.8 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.9 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l. .

SECTION D

IDENTIFICATION AND DETERMINATION OF SELECTED SEMIVOLATILE ORGANICS
IN SOIL AND SOLIDS: USATHAMA CERTIFIED METHOD L9 for UBTL;
USATHAMA CERTIFIED METHOD X9 FOR CAL; AND
USATHAMA CERTIFIED METHOD X9-A FOR HEA

DEVELOPED FROM
EPA METHOD 8270, SW-846, 2ND EDITION, JULY 1982

USATHAMA CERTIFIED METHOD L9 FOR UBTL

USATHAMA CERTIFIED METHOD
IDENTIFICATION AND DETERMINATION OF SELECTED SEMIVOLATILE ORGANICS
IN SOIL AND SOLIDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

I. APPLICATION

This method is designed as a semiquantitative method for the following semivolatile organic compounds in soil and solid samples based on solvent extraction and GC/MS determination (See Section VII for referenced Methods).

<u>Analyte</u>	<u>Molecular Formula</u>	<u>Melting Point (°C)</u>	<u>Boiling Point (°C)</u>
Aldrin	C ₁₂ H ₈ Cl ₆		
Endrin	C ₁₂ H ₈ Cl ₆ O		
Dieldrin	C ₁₂ H ₈ Cl ₆ O		
Isodrin	C ₁₂ H ₈ Cl ₆		
p,p'-DDT (1,1-Bis-(p-chlorophenyl)-2,2,2-trichloroethane)	C ₁₄ H ₉ Cl ₅		
p,p'-DDE (2,2-Bis-(p-chlorophenyl)-1,1-dichloroethylene)	C ₁₄ H ₈ Cl ₄		
CPMS (chlorophenyl methyl sulfide)	C ₇ H ₇ ClS		
CPMSO (chlorophenyl methyl sulfoxide)	C ₇ H ₇ ClSO		
CPMSO ₂ (chlorophenyl methyl sulfone)	C ₇ H ₇ ClSO ₂		
HCCPD (hexachlorocyclopentadiene)	C ₅ H ₆	-10	239
Oxathiane	C ₄ H ₈ SO		147
Dithiane	C ₄ H ₈ S ₂	110	200
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂		
Parathion	C ₁₀ H ₁₄ NO ₅ PS		
Chlordane	Technical Mixture		
Supona	C ₁₂ H ₁₄ Cl ₃ O ₄ P		
DIMP (diisopropyl methylphosphonate)	C ₇ H ₁₇ O ₃ P		
Atrazine	C ₈ H ₁₄ CLN ₃		
Vapona	C ₄ H ₇ Cl ₂ O ₄ P		
DBCP (dibromochloropropane)	C ₃ H ₅ Br ₂ Cl		
DCPD (dicyclopentadiene)	C ₁₀ H ₁₂	-1	170

A. Tested Concentration Range

The tested concentration range of the compounds extracted from standard soil and analyzed are as follows:

<u>Analyte</u>	<u>Tested Concentration Range (µg/g)*</u>
Oxathiane	0.25 - 99.5
DCPD	0.25 - 99.5
DIMP	0.25 - 99.5
Dithiane	0.25 - 99.5
DBCP	0.25 - 99.5
Vapona	0.25 - 99.5
CPMS	0.25 - 99.5
HCCPD	0.25 - 99.5
CPMSO	0.25 - 99.5
CPMSO2	0.25 - 99.5
Atrazine	0.25 - 99.5
Malathion	0.25 - 99.5
Aldrin	0.25 - 99.5
Parathion	0.25 - 99.5
Isodrin	0.25 - 99.5
Supona	0.25 - 99.5
p,p'-DDE	0.25 - 99.5
Dieldrin	0.25 - 99.5
Endrin	0.25 - 99.5
p,p'-DDT	0.25 - 99.5
Chlordane	0.25 - 99.5
Diethylphthalate-D ₄	0.25 - 99.5
2-Chlorophenol-D ₄	0.25 - 99.5
1,3-Dichlorobenzene-D ₄	0.25 - 99.5
Diethylphthalate-D ₄	0.25 - 99.5

*µg/g = micrograms per gram

B. Sensitivity

The extracted ion current area count responses at the detection limit on standard soil (Sec. I.C) are:

<u>Analyte</u>	<u>Quantitation Ion</u>	<u>Ion Peak Area Counts</u>	<u>Retention Time*</u>	<u>Relative Retention Time (RRT)</u>
Oxathiane	104	3100	7:54	0.357
2-Chlorophenol-D ₄	132	7100	10:05	0.456
1,3-Dichlorobenzene-D ₄	150	8100	10:26	0.472
Dicyclopentadiene	132	130	10:53	0.492
DIMP	123	4700	11:38	0.526
Dithiane	120	5300	11:39	0.527
DBCP	157	2500	11:59	0.542
Vapona	109	17700	14:46	0.668
CPMS	158	6800	15:09	0.685

Hexachlorocyclopentadiene	237	490	16:09	0.730
CPMSO	159	1000	18:33	0.839
CPMSO ₂	175	1460	19:09	0.866
Diethylphthalate-D ₄	153	6040	19:37	0.887
Atrazine	200	1440	21:38	0.979
Phenanthrene-D ₁₀	188	Internal Standard	22:07	1.000
Malathion	173	770	24:01	1.085
Parathion	291	330	24:20	1.100
Aldrin	263	604	24:19	1.099
Isodrin	193	1080	24:58	1.128
Supona	267	380	25:08	1.136
Chlordane	373	100	25:36	1.158
p,p'-DDE	246	2990	26:17	1.188
Dieldrin	79	1150	26:29	1.197
Endrin	263	60	26:56	1.218
p,p'-DDT	235	860	27:55	1.262
Diethylphthalate-D ₄	153	2550	32:11	1.455

*minutes:seconds

RRT = Retention time relative to d10-phenanthrene internal standard
(retention time = 22:07).

C. Certified Detection Limits

The detection limits in standard soil, calculated according to the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) detection limit program with 90-percent confidence limits (USATHAMA, 1982) are:

<u>Analyte</u>	<u>Detection Limit</u> <u>µg/g</u>	<u>Range</u> <u>µg/g</u>
Oxathiane	0.3	0.3 - 99.5
2-Chlorophenol-D ₄	1	1 - 99.5
1,3-Dichlorobenzene-D ₄	0.4	0.4 - 99.5
Dicyclopentadiene	1	1 - 50
DIMP	1	1 - 99.5
Dithiane	0.4	0.4 - 99.5
DBCP	0.3	0.3 - 99.5
Vapona	3	3 - 99.5
CPMS	0.9	0.9 - 99.5
Hexachlorocyclopentadiene	0.6	0.6 - 25.1
CPMSO	0.3	0.3 - 99.5
CPMSO ₂	0.3	0.3 - 99.5
Diethylphthalate-D ₄	0.3	0.3 - 99.5
Atrazine	0.3	0.3 - 99.5
Malathion	0.7	0.7 - 25.1
Parathion	0.9	0.9 - 25.1
Aldrin	0.3	0.3 - 99.5
Isodrin	0.3	0.3 - 25.1
Supona	0.6	0.6 - 25.1
Chlordane	2	2 - 25.1

p,p'-DDE	0.6	0.6 - 50
Dieldrin	0.3	0.3 - 99.5
Endrin	0.5	0.5 - 25.1
p,p'-DDT	0.5	0.5 - 25.1
Diethylphthalate-D ₄	0.6	0.6 - 99.5

D. Interferences

No interferences were encountered in standard soil samples. Precautions must be taken to prevent contamination artifacts. Coeluters with similar ions from field samples could interfere.

E. Analysis Rate

One sample extractor and one GC/MS operator can analyze eight samples in an eight-hour day if no significant amounts of background interferences are detected.

II. CHEMISTRYA. Chemical Abstract Service (CAS) Registry Numbers

<u>Analyte</u>	<u>CAS Registry Number</u>
Aldrin	309-00-2
Endrin	72-20-8
Dieldrin	60-57-1
Isodrin	465-73-6
p,p'-DDT	50-29-3
p,p'-DDE	72-55-9
CPMS (chlorophenyl methyl sulfide)	--
CPMSO (chlorophenyl methyl sulfoxide)	--
CPMSO ₂ (chlorophenyl methyl sulfone)	--
HCCPD (hexachlorocyclopentadiene)	77-47-4
Oxathiane	15980-15-1
Dithiane	505-29-3
Malathion	121-75-5
Parathion	56-38-2
Chlordane	57-74-9
Supona	2701-86-2
DIMP (diisopropyl methylphosphonate)	1912-24-9
Atrazine	62-73-7
Vapona	96-12-8
DBCP	77-73-6
DCPD (dicyclopentadiene)	

B. Chemical Reactions: N/A

III. APPARATUS

A. Instrumentation

A Finnigan Model 5100 (UBTL # MS-05) gas chromatograph-mass spectrometer equipped with a fused silica capillary column. The GC/MS system is coupled to an INCOS computer system. The system is operated in the electron impact ionization (EI) mode and tuned to comply with EPA ion abundance criteria (See Table 1) when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected as described in EPA Method 8270.

Table 1. DFTPP Key Ions and Ion Abundance Criteria

<u>Mass</u>	<u>Ion Abundance Criteria</u>
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

Varian Model 6000 gas chromatograph equipped with a fused silica capillary column and a flame-ionization detector is used for the GC-Screens. The GC is coupled to a strip-chart recorder in addition to a Hewlett Packard 3357 Laboratory Data System.

B. GC/MS Parameters

EPA Method 625 (EPA, 1984) for semivolatiles attached to this method (Attachment 1), describes the recommended GC/MS parameters, hardware, glassware, and reagents used in this procedure.

1. The GC conditions for the GC/MS are:

Column:	30m by 0.25 mm (id) DB5 (0.25 μ m coating) fused silica.
Temperature Program:	Held isothermal at 45 °C for 4 min and then programmed at 10 °C/min to 280 °C.
Injector Temperature:	290 °C

Transfer Line: 290 °C
Carrier Gas: Helium at about 30 cm/sec
Electron Energy: 70 ev
Run Time: 34 minutes

2. GC Screen:

Column: 30m x 0.32mm (1 µm film thickness)
silicone coated, fused silica
capillary column (DB-5 or equivalent).

Temperature Program: Initial column temperature is held
isothermal at 60 °C for 4 minutes and
temperature programmed at 8 °C/minute
to 280 °C. The temperature is held at
280 °C for 8 minutes.

Injector Temperature: 290 °C

Detector Temperature: 290 °C

Carrier Gas: Helium at about 30 cm/sec

3. Injection Volume: 2 µL

4. Retention Times (GC/MS): See I.B. above.

C. Hardware/Glassware:

1. Sample containers, as appropriate.
2. Soxhlet extractors and associated equipment.
3. K-D concentrators, Snyder columns and heated water bath.
4. Volumetric flasks, pipettes, and syringes, as necessary.
5. Forty mL vials with phenolic screw caps containing Teflon liners.

D. Reagents:

1. Dichloromethane, acetone, and toluene: Burdick and Jackson Pesticide Quality or equivalent.
2. Analytical reference standards of each analyte. Malathion, Parathion, Isodrin, Supona, and Atrazine are from EPA (Reference Standards Repository, RTP-N.C.); Vapona is from CSI Lot 2-37B 98%; all others are USATHAMA SARMS or interim SARMS.

3. Decafluorotriphenylphosphine (DFTPP): Aldrich Chemical Lot 1524 CEJ.
4. d4-1,3-Dichlorobenzene, d4-Diethylphthalate, d4-Di-n-octylphthalate and d4-2-Chlorophenol as surrogates from USATHAMA as SARMS.
5. d10-Phenanthrene as an internal standard (KOR Isotopes Lot NL166).
6. Phenanthrene as GC Screen standard (Aldrich Chemical).
7. Anhydrous sodium sulfate (dichloromethane rinsed).

IV. STANDARDS

A. Calibration Standards

1. Stock Solutions

Primary stock solutions of each analyte, surrogate, and the d10-phenanthrene internal standard are prepared at 10 mg/mL in dichloromethane. Atrazine is prepared at 5 mg/mL in dichloromethane due to low solubility. At 10 mg/mL, dithiane requires extensive sonication for complete dissolution.

All solutions are prepared in 10 mL volumetric flasks and then transferred to 15 mL amber vials with Teflon-lined screw caps, or Teflon-faced septa and screw caps. The vials are stored and refrigerated at 4 °C.

2. GC/MS Working Standards

The stock solutions of analytes and surrogates are combined and diluted in dichloromethane according to the following table:

<u>Preparation</u>	<u>Nominal Final Concentration</u>
1.50 mL each stock / 100 mL	150 µg/mL
25 mL of 150 µg/mL / 100 mL	37.5 µg/mL
20 mL of 37.5 µg/mL / 100 mL	7.5 µg/mL
50 mL of 7.5 µg/mL / 100 mL	3.75 µg/mL

3. Surrogate Spike Standard

The analytical stock surrogate solutions (10 mg/mL) are combined and diluted in dichloromethane according to the following schedule:

<u>Preparation</u>	<u>Nominal Final Concentration</u>
1.50 mL each stock / 100 mL	150 µg/mL

4. GC/MS Internal Standard

The stock solution of d10-phenanthrene (10 mg/mL) is diluted in dichloromethane as follows:

<u>Preparation</u>	<u>Nominal Final Concentration</u>
2.0 mL of 10 µg/mL / 10 mL	2.0 mg/mL

5. GC/MS Calibration Standards

One milliliter aliquots of each GC/MS working standard are spiked with 25 µL of the GC/MS internal standard solution (2.0 mg/mL).

B. Control Spikes

Aliquots of the GC/MS working standards are spiked onto 15 g standard soil samples (previously placed in extraction thimbles in soxhlet extractors) according to the following schedule:

<u>Level</u>	<u>mL of Spike Std. Added</u>	<u>Final Concentration for 15.0 g soil - µg/g</u>
0	0	0
.5X	1 mL of 3.75 µg/mL	.25
1X	1 mL of 7.5 µg/mL	.50
2X	2 mL of 7.5 µg/mL	1.0
5X	1 mL of 37.5 µg/mL	2.5
10X	2 mL of 37.5 µg/mL	5.0
20X	1 mL of 150 µg/mL	10.0
50X	2.5 mL of 150 µg/mL	25
100X	5 mL of 150 µg/mL	50
200X	10 mL of 150 µg/mL	100

For the purposes of certification, no GC/FID screens need be employed.

C. Daily GC Spikes

For each lot, one 15 g portion of standard soil will be spiked in the soxhlet thimble with one mL of the 150 µg/mL surrogate spike standard which contains each of the four deuterated surrogates at a concentration of 150 µg/mL. The resulting soil spike contains each surrogate at a level of 10 µg/g.

V. PROCEDUREA. Quality Assurance

Each soil sample will be spiked in the soxhlet thimble with the analytical surrogate spike standard. A 1 mL aliquot of the standard will be added to each 15 g soil sample to give a 10 µg/g surrogate concentration. Each sample lot will also include a reagent blank and a standard soil method blank.

B. Extraction

Subsamples (15 g weighed \pm 0.1 g) are placed in clean (Soxhlet extracted) paper thimbles, mixed with 30 g of anhydrous sodium sulfate and spiked with the surrogate standards. The spiked soil is allowed to stand for at least one hour and then is extracted for eight hours with 300 mL of dichloromethane. The extracts are concentrated with a K-D apparatus to a temporary final volume of 10 mL for GC-FID screening. Any further concentrations are done under nitrogen.

C. GC-FID Screening

The GC-FID attenuation is adjusted so that a 2 μ L injection of the 15 μ g/mL phenanthrene standard gives about 50% full-scale deflection. The sample extracts from V-B above are analyzed by GC-FID using 2 μ L hand injections (no autosampler) to determine whether the extracts will require either concentration or dilution such that the largest GC-FID peaks will not exceed the highest (150 μ g/mL) GC/MS analyte standards. For example, if there are no GC-FID peaks greater than the 15 μ g/mL screen standard, the sample extract can be concentrated to 1.0 mL final volume; this will allow the detection limits to be met while not generating analyte peaks greater than the highest GC/MS standards.

D. GC/MS Calibration

Response factors (RFs) and a standard curve for each analyte and each surrogate are developed via the dl0-phenanthrene internal standard by injection of the four "GC/MS Standards" (IV.A.2. above). The response factors are updated daily, before the analysis of sample extracts, using the middle (37.5 μ g/mL) standard mix. If the daily calibration RFs differ (using "%D" as defined below) from the average RFs by more than 25% for any of the surrogates then a new standard curve and new set of average response factors must be made. If the daily calibration is within the acceptable "%D" window, then analysis of the sample extracts can proceed.

The percent difference (%D) calculation is $[(\text{daily RF} - \text{average RF}) / \text{average RF}] \times 100$. Calculation and tabulation of daily RFs, average RF's, and "%D" are easily done with INCOS or equivalent software.

The GC/MS system is tuned daily to meet EPA criteria for DFTPP (See Table 1.1).

E. GC/MS Analysis

After demonstration of acceptable calibration, the screened extracts are analyzed by GC/MS. Just prior to analysis, a 25 μ L aliquot of the dl0-phenanthrene internal standard is added to 1.0 mL of the sample extract, yielding an internal standard concentration of 50 μ g/mL.

F. Unknown GC/MS Peaks

Unknown GC/MS peaks will be tentatively identified by computer assisted comparison to the NBS 31,000 entry mass spectral library. The mass spectroscopist will use the INCOS "fit," "purity," and "refit" criteria to assign probabilities of correct structural assignment. Hardcopy mass spectra of all unknowns will be provided with the report.

The largest five unknown peaks which are present in excess of ten percent of the area of the m/e 188 peak for d10-phenanthrene internal standard will be library searched.

VI. CALCULATIONS

$$A. \quad \mu\text{g analyte/mL extract} = \frac{(\text{area of analyte peak}) (50 \mu\text{g/mL IS})}{(\text{area of I.S.}) (\text{analyte RF})}$$

Where I.S. = d-10 phenanthrene internal standard

$$\text{RF} = \text{Response Factor} \quad \frac{(\text{area of analyte peak}) (50 \mu\text{g/mL I.S.})}{(\text{area of I.S.}) (\text{conc. of analyte})}$$

$$B. \quad \mu\text{g analyte/g sample} = \text{ppm} = \frac{\mu\text{g analyte/mL extract}}{\text{g sample/mL extract}}$$

C. The calculated result is corrected for recovery (as determined during certification) and reported on a dry weight basis.

VII. REFERENCES

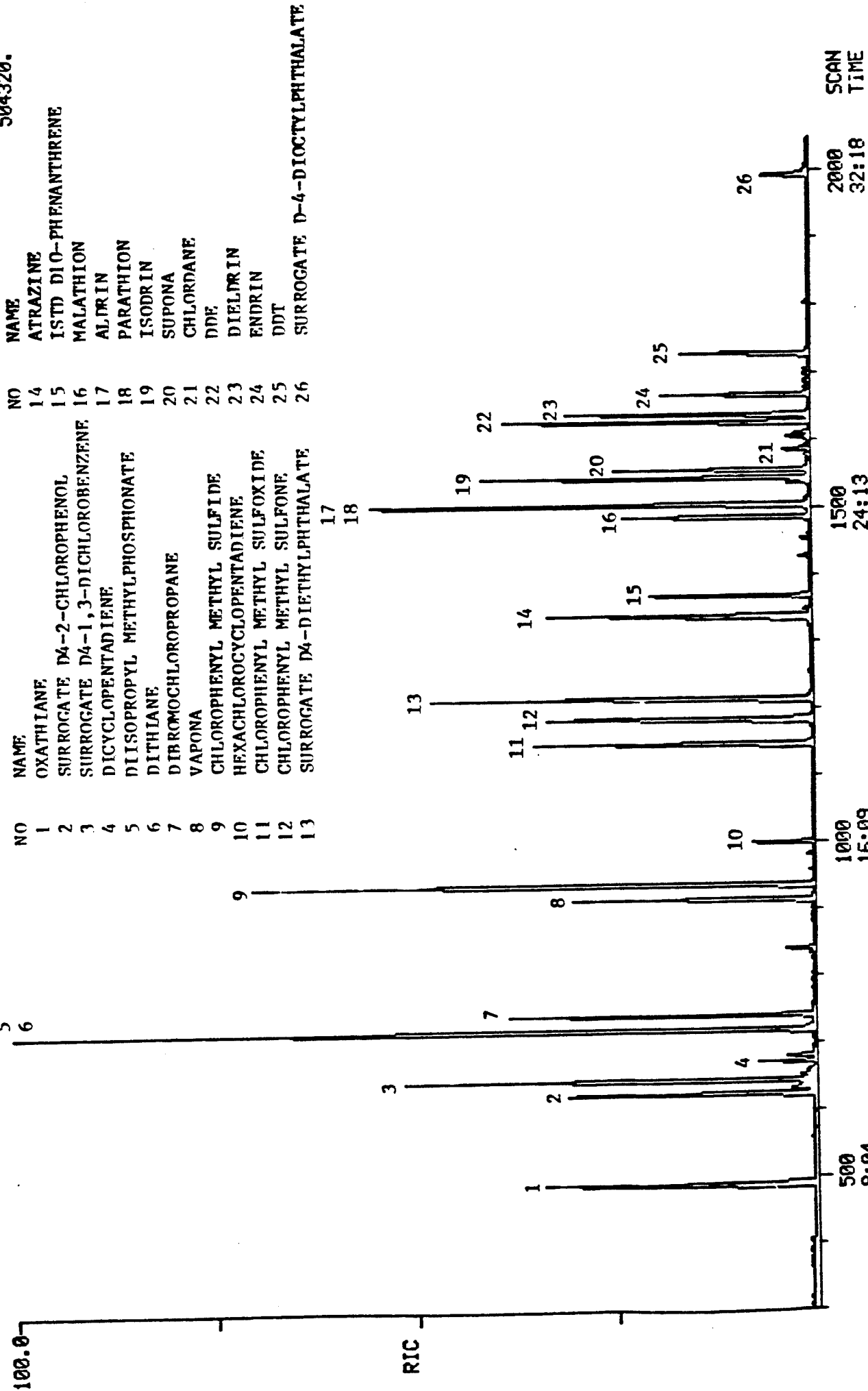
Copies of EPA Methods 3540 and 8270 (Test Methods for Evaluating Solid Waste, US EPA SW-846, 2nd Edition, July 1982) are attached.

.RIC
 04/11/85 11:15:00
 SAMPLE:
 CONDS.:
 RANGE: G 1.2850

DATA: F10251
 CALI: F102515. "2
 SCANS 300 TO 2050

LABEL: N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20, 3

504320.



UBTL SEMI-VOLATILE ORGANICS (19)

<u>Name</u>	<u>Code</u>	<u>Accuracy</u>	<u>Range</u>
Oxathiane	OXAT	0.846	0.3-99.5
Surrogate D4-2-Chlorophenol	2CLPD4	1.091	1-99.5
Surrogate D4-1,3-Dichlorobenzene	13DBD4	0.828	0.4-99.5
Dicyclopentadiene	DCPD	1.029	1-50
Diisopropyl methylphosphonate	DIMP	0.998	1-99.5
Dithiane	DITH	0.846	0.4-99.5
Dibromochloropropane	DBCP	0.854	0.3-99.5
Vapona	DDVP	0.999	3-99.5
Chlorophenyl methylsulfide	CPMS	0.997	0.9-99.5
Hexachlorocyclopentadiene	CL6CP	0.823	0.6-25.1
Chlorophenyl methylsulfoxide	CPMSO	0.999	0.3-99.5
Chlorophenyl methylsufone	CPMSO2	0.962	0.3-99.5
Surrogate D4-Diethylphthalate	DEPD4	1.035	0.3-99.5
Atrazine	ATZ	1.132	0.3-99.5
Malathion	MLTHN	1.092	0.7-25.1
Aldrin	ALDRN	0.881	0.3-99.5
Parathion	PRTHN	1.047	0.9-25.1
Isodrin	ISODR	0.978	0.3-25.1
Supona	SUPONA	1.023	0.6-25.1
Chlordane	CLDAN	0.939	2-25.1
DDE	PPDDE	1.086	0.6-50
Dieldrin	DLDRN	1.048	0.3-99.5
Endrin	ENDRN	0.942	0.5-25.1
DDT	PPDDT	0.983	0.5-25.1
Surrogate D4-Dioctylphthalate	DNOPD4	1.022	0.6-99.5

METHOD 3540

SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

2 / WORKUP TECHNIQUES - Organic

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

2 / ORGANIC ANALYTICAL METHODS - GC/MS

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- μ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- μ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ($\pm 2^\circ$ C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ± 0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4 / ORGANIC ANALYTICAL METHODS - GC/MS

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^a

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

^aJ.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

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5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D₁₀-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be used in place of D₁₂-benzo(a)pyrene.

5.9 Column performance standards: D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D₃-phenol, D₈-naphthalene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. D₁₀-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D₅-phenol or D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

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$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_S = Response for the parameter to be measured.

A_{IS} = Response for the internal standards.

C_{IS} = Concentration of the internal standard in $\mu\text{g/l}$.

C_S = Concentration of the compound to be measured in $\mu\text{g/l}$.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{IS} , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 $\mu\text{g/ml}$ of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2Cl_2 and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4 , the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- μ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

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was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_c(7.3.8)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{\text{GPC}}(7.3.7)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

V_s = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_c(7.3.8)$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within ± 15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within $\pm 20\%$ of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$ = internal standard concentration factor calculated in Section 7.3.8.

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in $\mu\text{g/g}$ without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ($s/R \times 100$) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D10-phenanthrene.

USATHAMA CERTIFIED METHOD X9 FOR CAL

USATHAMA CERTIFIED METHOD#X9
Identification and Determination of Selected Semivolatile
Organics in Soil and Solids

(CAL Version 6, 5/4/85)
(USATHAMA Version 2, 5/4/85)

- I. Application: This method is designed as a semiquantitative method for selected semivolatile organic compounds in soil and solid samples based on solvent extraction and GC/MS determination (EPA Methods 3540 and 8270). The method is certified as semiquantitative based on a standard reference soil.

A. Tested Concentration Ranges:
0.25 to 100 ug/g (see I-C, below)

B. Sensitivity:

Analyte	RRT	Fragment ion	Sensitivity	
			Ion Peak Area	Conc. (ug/g)
OXAT	0.270	104	79,000	6
DCPD	0.424	132	1,540	0.4
DIMP	0.468	123	4,680	0.3
DITH	0.461	120	92,000	7
DBCP	0.480	157	1,984	0.3
DDVP	0.632	109	5,386	0.3
CPMS	0.644	158	45,000	4
CL6CP	0.697	237	830	0.3
CPMSO	0.818	159	24,000	7
CPMSO2	0.850	175	1,550	0.6
ATZ	0.985	200	1,100	0.3
MLTHN	1.112	173	860	0.3
ALDRN	1.112	263	550	0.3
PRTHN	1.123	291	390	0.3
ISODR	1.144	193	730	0.3
Supona	1.167	267	760	0.3
PPDDE	1.222	246	1,370	0.3
DLDRN	1.224	79	1,500	0.3
ENDRN	1.245	263	240	0.3
PPDDT	1.303	235	2,100	0.6
CLDAN	1.182	373	80	0.6
2CLPD4	0.370	132	74,285	10
13DBD4	0.390	150	111,047	10
DEPD4	0.880	153	118,104	10
DNOPD4	1.460	153	165,116	10

RRT = Retention time relative to d10- phenanthrene
internal standard (retention time = 19.11 min.).

C. Certified Detection Limits, Ranges and Accuracy:

Analyte	Detection Limit (ug/g)	Upper Concentration Range (ug/g)	Accuracy
OXAT	6	50	0.547
DCPD	0.4	50	0.836
DIMP	0.3	100	0.627
DITH	7	50	0.740
DBCP	0.3	50	0.837
DDVP	0.3	100	1.00
CPMS	4	50	1.05
CL6CP	0.3	100	0.882
CPMSO	7	100	1.11
CPMSO2	0.6	100	1.05
ATZ	0.3	100	0.828
MLTHN	0.3	100	1.08
ALDRN	0.3	100	0.596
PRTHN	0.3	100	0.521
ISODR	0.3	100	0.766
Supona	0.3	100	0.614
PPDDE	0.3	100	0.666
DLDRN	0.3	100	0.935
ENDRN	0.3	50	0.460
PPDDT	0.6	100	0.645
CLDAN	0.6	100	0.494
2CLPD4	4	20	0.701
13DBD4	1	20	0.950
DEPD4	2	20	0.993
DNOPD4	1	20	1.16

D. Interferences: Coeluters with similar ions could interfere.

E. Analysis Rate: One sample extractor and one GC/MS operator can analyze eight samples in an eight hour day.

II. ChemistryA. Alternate Nomenclature and Chemical Abstracts Registry Numbers:

ALDRN	(Aldrin)	309-00-2
ENDRN	(Endrin)	72-20-8
DLDRN	(Dieldrin)	60-57-1
ISODR	(Isodrin)	465-73-6
PPDDT	(DDT)	50-29-3
PPDDE	(DDE)	72-55-9

CPMS	(chlorophenyl methyl sulfide)	
CPMSO	(chlorophenyl methyl sulfoxide)	
CPMSO2	(chlorophenyl methyl sulfone)	
CL6CP	(hexachlorocyclopentadiene)	77-47-4
OXAT	(Oxathiane)	15980-15-1
DITH	(Dithiane)	505-29-3
MLTHN	(Malathion)	121-75-5
PRTHN	(Parathion)	56-38-2
CLDAN	(Chlordane)	57-74-9
	(Supona)	2701-86-2
DIMP	(diisopropyl methylphosphonate)	1912-24-9
ATZ	(Atrazine)	62-73-7
DDVP	(Vapona)	96-12-8
DBCP	(1,2-dibromo-3-chloropropane)	77-73-6
DCPD	(dicyclopentadiene)	
2CLPD4	(2-chlorophenol-d4)	
13DBD4	(1,3-dichlorobenzene-d4)	
DEPD4	(diethyl phthalate-d4)	
DNOPD4	(di-n-octyl phthalate-d4)	

B. Physical and Chemical Properties:

ALDRN:	$C_{12}H_8Cl_6$,
ENDRN:	$C_{12}H_8Cl_6O$,
DLDRN:	$C_{12}H_8Cl_6O$,
ISODR:	$C_{12}H_8Cl_6$,
PPDDT:	$C_{14}H_9Cl_5$,
PPDDE:	$C_{14}H_8Cl_4$,
CPMS:	C_7H_7ClS ,
CPMSO:	C_7H_7ClSO ,
CPMSO2:	$C_7H_7ClSO_2$,
CL6CP:	C_5Cl_6 mp-10, bp239
OXAT:	C_4H_8SO , bp147
DITH:	$C_4H_8S_2$, mp110, bp200
MLTHN:	$C_{10}H_{19}O_6PS_2$,
PRTHN:	$C_{10}H_{14}NO_5PS$,
CLDAN:	mixture
Supona:	$C_{12}H_{14}Cl_3O_4P$,
DIMP:	$C_7H_{17}O_3P$
ATZ:	$C_8H_{14}ClN_5$,
DDVP:	$C_4H_7Cl_2O_4P$,
DBCP:	$C_3H_5Br_2Cl$,
DCPD:	$C_{10}H_{12}$, mp-1

C. Chemical Reactions: N/A

III. Apparatus

- A. Instrumentation: Finnigan Model 1020 (or equivalent) gas chromatograph-mass spectrometer equipped with a fused silica capillary column. The GC/MS system is coupled to an INCOS computer system (or equivalent). The system is operated in the EI mode and tuned as described in EPA Method 8270.

Varian Model 3700 (or equivalent) gas chromatograph equipped with a flame-ionization detector is used for the GC-Screens. The GC is coupled to a strip-chart recorder.

B. Parameters:

1. GC/MS:
 - a. Column: 30m by 0.25mm (id) DB5 (25um coating) fused silica held isothermal at 45°C for 4 min and then programmed at 10°C/min to 280°C.
 - b. Conditions: Injector port: 300°C; transfer line: 300°C; carrier gas (helium) at about 30 cm/sec; electron energy: 70 ev.
2. GC Screen:
 - a. Column: 1.5m by 2mm (id) glass column packed with 1% SP1240DA held isothermal at 60°C for 2 min and temperature programmed at 8°C/min to 180°C. Any packed column run under appropriate conditions which provides the GC Screen data outlined in V-C (below) may be substituted.
 - b. Conditions: Injector port: 290°C; detector: 290°C; carrier gas (nitrogen) at about 25 mL/min.
3. Injection Volume: 2.0 uL
4. Retention Times (GC/MS): See I-B above.

C. Hardware/Glassware:

1. Sample containers, as appropriate.
2. Soxhlet extractors and associated equipment.
3. K-D concentrators, Snyder columns and heated water bath.
4. Volumetric flasks and pipettes as necessary.
5. Test tubes.

D. Chemicals:

1. Dichloromethane: Burdick and Jackson Pesticide Quality or equivalent.
2. Analytical reference standards of each analyte. Malathion, Parathion, Azodrin, Supona, Vapona, and Atrazine are from EPA (Reference Standards Repository, RTP-N.C.); all others are USATHAMA SARMS or interm SARMS.
3. Decafluorotriphenylphosphine (DFTPP).
4. d4-1,3-dichlorobenzene, d4-diethylphthalate, d4-di-n-octylphthalate and d4-2-chlorophenol as surrogates from USATHAMA as SARMS.
5. d10-Phenanthrene as an internal standard (Cambridge Isotope Labs).
6. Phenanthrene as GC Screen standard (Aldrich Chemical).
7. Anhydrous sodium sulfate (dichloromethane rinsed).

IV. Standards

- A. Stock Solutions: Stock solutions of analytes, phenanthrene, d10-phenanthrene, and surrogates are prepared in 10 mL volumetric flasks at 10.0 mg/mL in dichloromethane and stored at 4°C in the dark. Since dichloromethane is volatile, care must be taken to monitor potential loss of solvent during storage.
- B. GC/MS Working Standards: The stock analyte and surrogate solutions are combined and diluted in dichloromethane to give 3.75 ug/mL, 7.50 ug/mL, 37.5 ug/mL and 150 ug/mL concentrations of analytes and surrogates. In addition, 50 uL of the d10-phenanthrene internal standard stock solution is added to 10 mL of each final GC/MS working standard, as follows:

Code	Preparation	ug/mL conc.		
		Analytes	Surr.	I.S.
625-WS-G	1.50 mL each stock, dil. to 100 mL, save 10 mL	150	150	50
625-WS-E	25 mL of 625-WS-G, dil. to 100 mL, save 10 mL	37.5	37.5	50
625-WS-C	20 mL of 625-WS-E, dil. to 100 mL, save 10 mL	7.50	7.50	50
625-WS-B	50 mL of 625-WS-C, dil. to 100 mL, save 10 mL	3.75	3.75	50

- C. Surrogate Spike Standards: The stock surrogate solutions are combined and diluted in dichloromethane to give 150 ug/mL concentrations of each surrogate. The solution is labelled 625-SUR-G.
- D. GC/MS Internal Standard: The stock solution of d10-phenanthrene (internal standard) is diluted in dichloromethane to give a 2.0 mg/mL solution. A 25 uL aliquot is added to 1.0 mL of final sample extract just prior to GC/MS analysis, yielding the internal standard at 50 ug/mL concentration.
- E. GC Screen Standard: The stock solution of unlabelled phenanthrene is diluted in dichloromethane to give a 15 ug/mL GC Screen Standard.
- F. Certification Standards: For the purpose of certification on standard RMA soil, a series of analyte/surrogate spiking standards are prepared as described in IV-B above (in fact, the exact same solutions without internal standard are prepared). Aliquots (1.0 mL to 10 mL) are added to 15g of standard soil and processed as in V (below) as follows:

Sample	ug/g spike	mL of spike std. (conc) added	Soil Extract final volume
control	0.0	NONE	1.0 mL
0.5x	0.25	1.0 mL 625-SS-B (3.75 ug/mL)	1.0 mL
1x	0.50	1.0 mL 625-SS-C (7.5 ug/mL)	1.0 mL
2x	1.0	1.0 mL 625-SS-D (15 ug/mL)	1.0 mL
5x	2.5	1.0 mL 625-SS-E (37.5 ug/mL)	1.0 mL
10x	5.0	1.0 mL 625-SS-F (75 ug/mL)	1.0 mL
20x	10	1.0 mL 625-SS-G (150 ug/mL)	1.0 mL
50x	25	2.5 mL 625-SS-G (150 ug/mL)	10 mL
100x	50	5.0 mL 625-SS-G (150 ug/mL)	10 mL
200x	100	10 mL 625-SS-G (150 ug/mL)	50 mL

The final volumes noted will keep the analytes and surrogates within the 3.75 ug/mL to 150 ug/mL GC/MS working standard concentration range. The use of dilutions is legitimate in view of the GC-FID screen which will be used for real samples. For the purpose of certification, no GC-FID screens need be employed.

V. Procedures:

- A. Quality Assurance: Each soil sample is spiked with 1.0 mL of solution 625-SUR-G, yielding each surrogate at 10 ug/g (ppm). In addition, one standard soil "method blank" is spiked in the same fashion for each sample set (recoveries from this sample are used for X-bar quality control charts).
- B. Extraction: Subsamples (15 g weighed + 0.1 g) are placed in clean (Soxhlet extracted) paper thimbles, mixed with 30 g of anhydrous sodium sulfate, spiked with the surrogate standards, and extracted for eight hours with 300 mL of dichloromethane. The extracts are concentrated with a K-D setup to a temporary final volume of 10 mL for GC-FID screening. Any further concentrations are done under nitrogen.
- C. GC-FID Screening: The GC-FID attenuation is adjusted so that a 2 uL injection of the 15 ug/mL phenanthrene standard gives about 50% full-scale deflection. The sample extracts from V-A above are analyzed by GC-FID using 2 uL hand injections (no autosampler) to determine whether the extracts will require either concentration or dilution such that the largest GC-FID peaks will not exceed the highest (150 ug/mL) GC/MS analyte standards. For example, if there are no GC-FID peaks greater than the 15 ug/mL screen standard, the sample extract can be concentrated to 1.0 mL final volume; this will allow the detection limits to be met while not generating analyte peaks greater than the highest GC/MS standards.
- D. GC/MS Calibration: Response factors (RFs) and a standard curve for each analyte and each surrogate are developed via the d10-phenanthrene internal standard by 2 uL injections of the four "GC/MS Standards" (IV-B, above). The response factors are updated daily, before the analysis of sample extracts, using the middle (37.5 ug/mL) standard mix. If the daily calibration RFs differ (using "%D" as defined below) from the average RFs by more than 25% for any of the surrogates then a new standard curve and new set of average response factors must be made. If the daily calibration is

within the acceptable "%D" window, then analysis of the sample extracts can proceed.

The percent difference (%D) calculation is $[(\text{daily RF} - \text{average RF}) / \text{average RF}] \times 100$. Calculation and tabulation of daily RFs, average RF's, and "%D" are easily done with INCOS or equivalent software.

The GC/MS system is tuned to meet EPA criteria for DFTPP daily, as described in EPA Method 8720 (attached).

- E. GC/MS Analysis: After demonstration of acceptable linearity, the screened extracts are analyzed by GC/MS. Just prior to analysis, 25 uL of the d10-phenanthrene internal standard is added to 1.0 mL of the sample extract.
- F. Unknown GC/MS Peaks: Unknown GC/MS peaks will be tentatively identified by computer assisted comparison to the NBS 31,000 entry mass spectral library (or equivalent). The mass spectroscopist will use the INCOS (or equivalent) "fit", "purity" and "refit" criteria to assign probabilities of correct structural assignment. Hardcopy mass spectra of all unknowns will be provided with the report.

The five largest unknown peaks which are present in excess of ten percent of the area of the m/e 188 peak for d10-phenanthrene internal standard will be library searched.

VI. Calculations:

$$A. \text{ ug analyte/mL extract} = \frac{(\text{area of analyte peak})(50 \text{ ug/mL IS})}{(\text{area of I.S.})(\text{analyte RF})}$$

Where I.S.=d-10 phenanthrene internal standard

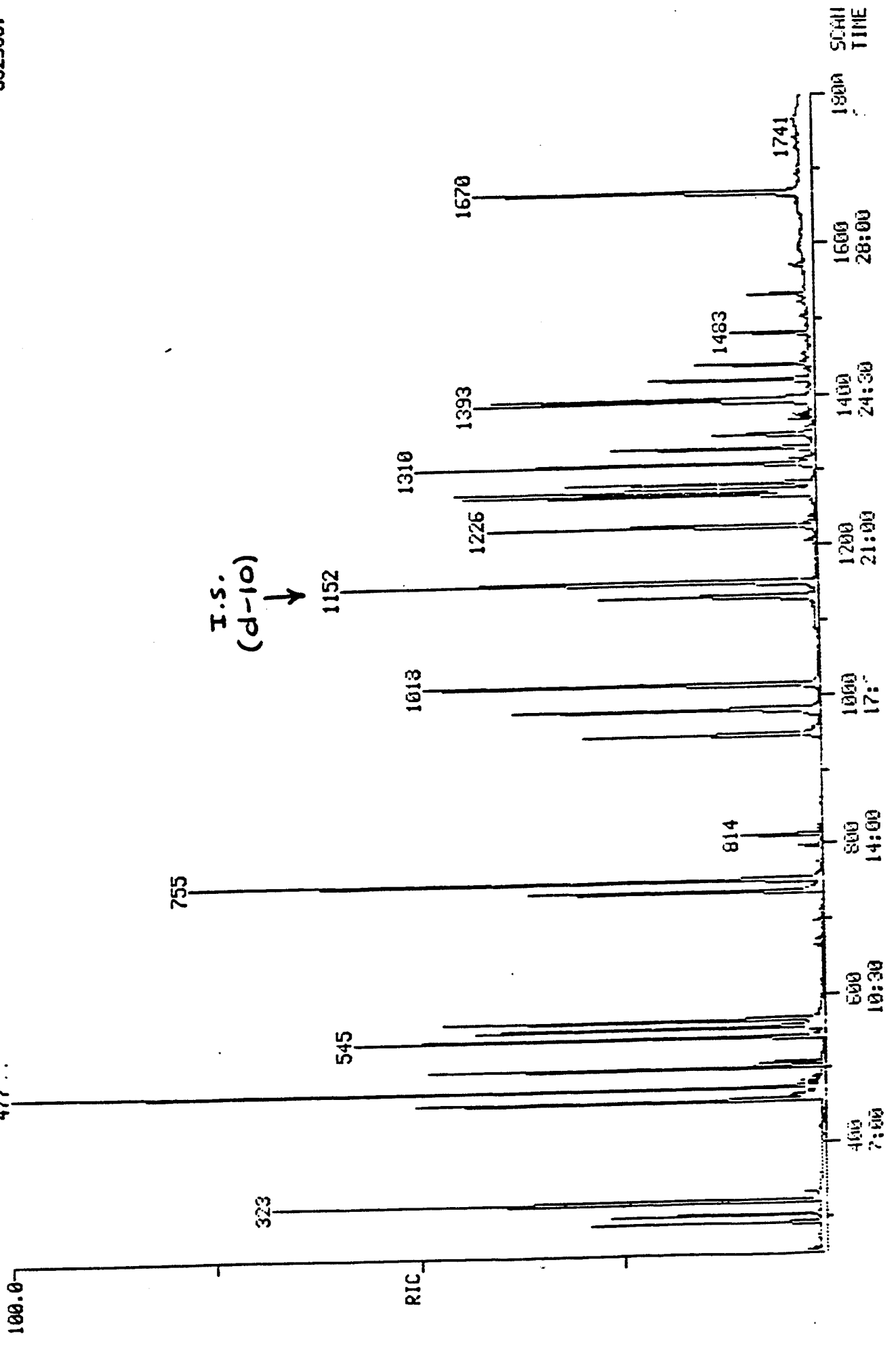
$$RF = \text{Response factor} = \frac{(\text{area of analyte peak})(50 \text{ ug/mL I.S.})}{(\text{area of I.S.})(\text{conc. of analyte})}$$

$$B. \text{ ug analyte/g sample} = \text{ppm} = \frac{\text{ug analyte/mL extract}}{\text{g sample/mL extract}}$$

- C. Final results are corrected for percent recovery (using the certified accuracy data) and for percent moisture to a dry weight basis.

VII References: Copies of EPA Methods 3540 and 8270 (Test Methods for Evaluating Solid Waste, US EPA SW-846, 2nd Edition, July 1982) are attached.

DATA: ST5850513 #1
CALI: FC435 #15
SCANS 250 TO 1800
552960.



METHOD 3540
SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet-extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

2 / WORKUP TECHNIQUES - Organic

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples:

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- μ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- μ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ($\pm 2^\circ$ C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ± 0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^a

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

^aJ.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D₁₀-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be used in place of D₁₂-benzo(a)pyrene.

5.9 Column performance standards: D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D₃-phenol, D₈-naphthalene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. D₁₀-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D₅-phenol or D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standards.

C_{is} = Concentration of the internal standard in $\mu\text{g/l}$.

C_s = Concentration of the compound to be measured in $\mu\text{g/l}$.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 $\mu\text{g/ml}$ of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2Cl_2 and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4 , the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- μ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{\text{GPC}(7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

V_s = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{c(7.3.8)}$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within ± 15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within $\pm 20\%$ of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$ = internal standard concentration factor calculated in Section 7.3.8.

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in $\mu\text{g/g}$ without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ($s/R \times 100$) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

USATHAMA CERTIFIED METHOD X9-A FOR HEA

**SEMIQUANTITATIVE DETERMINATION FOR SELECTED
SEMIVOLATILES IN SOIL AND SOLIDS
(Hittman Ebasco Associates, Inc.)**

- I. **APPLICATION:** This method covers the semiquantitative determination of selected semivolatile organic compounds in soil and solid samples using a solvent extraction and GC/MS analysis. The method described is a modification of EPA Methods 3540 and 8270.

A. Tested Concentration Ranges:

0.25 to 100 ug/g (See I-C).

B. Sensitivity:

Analyte	RRT	Fragment ion	Sensitivity	
			Ion Peak Area	Conc. (ug/g)
OXAT	0.346	104	431	0.9
DCPD	0.488	132	232	1.0
DIMP	0.521	123	932	0.8
DMMP	0.340	94	642	2.0
DITH	0.521	120	612	0.3
DBCP	0.538	157	428	0.3
DDVP	0.667	109	1430	0.6
CPMS	0.683	158	849	0.5
CL6CP	0.731	237	430	0.3
CPMSO	0.837	159	605	0.6
CPMSO2	0.863	175	580	0.7
ATZ	0.977	200	485	3.0
MLTHN	1.088	173	538	0.4
ALDRN	1.099	263	303	0.6
PRTHN	1.102	291	203	0.6
ISODR	1.128	193	324	0.5
Supona	1.138	267	397	0.3
PPDDE	1.189	246	522	0.9
DLDRN	1.196	79	652	0.8
ENDRN	1.217	263	625	0.6
PPDDT	1.261	235	563	0.3
CLDAN	1.159	373	530	2.0
2CLPD4	0.450	132	399	1.0
13DBD4	0.466	150	419	5.0
DEPD4	0.889	153	973	0.4
DNOPD4	1.428	153	1679	0.8

RRT = Retention time relative to d10- phenanthrene internal standard (retention time = 21.46 min.).

C. Certified Detection Limits, Ranges and Accuracy:

<u>Analyte</u>	<u>Detection Limit (ug/g)</u>	<u>Concentration Range (ug/g)</u>
Oxathiane	0.9	0.9-100
DCPD	1.0	1.0-50
DIMP	0.8	0.8-50
DMMP	2.0	2.0-50
Dithiane	0.3	0.3-100
DBCP	0.3	0.3-100
Vapona	0.6	0.6-100
CPMS	0.5	0.5-50
HCCPD	0.3	0.3-100
CPMSO	0.6	0.6-100
CMPSO2	0.7	0.7-100
Atrazine	3.0	3.0-90
Malathion	0.4	0.4-50
Aldrin	0.6	0.6-100
Parathion	0.6	0.6-50
Isodrin	0.5	0.5-100
Supona	0.3	0.3-100
DDE	0.9	0.9-100
Dieldrin	0.8	0.8-100
Endrin	0.6	0.6-100
DDT	0.3	0.3-100
Chlordane	2.0	2.0-30
1,3-Dichlorobenzene-d4	5.0	5.0-100
Diethyphthalate-d4	0.4	0.4-100
Diocetylphthalate-d4	0.8	0.8-100
Chlorophenol-d4	1.0	1.0-25

D. Interferences:

1. The use of high purity reagents and solvents minimizes interference problems.
2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences vary considerably from source to source.
3. Other interferences may be a result of contaminants in glassware, reagents, solvents or other sample processing hardware. These apparatus and materials must be routinely shown to be free of interferences under the conditions of the analysis by running laboratory method blanks.

- E. Analysis Rate: One sample extractor and one GC/MS operator can analyse eight samples in an eight hour day.

II. CHEMISTRY:

A. Alternate Nomenclature and Chemical Abstracts Registry Number:

<u>Code</u>	<u>Analyte</u>	<u>CAS No.</u>
OXAT	Oxathiane	15980-15-1
DCPD	Dicyclopentadiene	77-73-6
DIMP	Diisopropyl methylphosphonate	
DMMP	Dimethyl methyl phosphonate	505-29-3
DITH	Dithiane	96-12-8
DBCP	Dibromo chloro propane	62-73-7
DDVP	Vapona Dichlorvos	
CPMS	Chlorophenyl methyl sulfide	77-47-4
CL6CP	Hexachlorocyclopentadiene	
CPMSO	Chlorophenyl methyl sulfoxide	
CPMSO2	Chlorophenyl methyl sulfone	
ATZ	Atrazine	1912-24-9
MLTHN	Malathion	121-75-5
ALDRN	Aldrin	309-00-2
PRTN	Parathion	56-38-2
ISODR	Isodrin	465-73-6
Supona	Chlorfenvinphos	2701-86-2
PPDDE	DDE	72-55-9
DLDRN	Dieldrin	60-57-1
ENDRN	Endrin	72-20-8
PPDDT	DDT	50-29-3
CLDAN	Chlordane	57-74-9
2CLPD4	2-Chlorophenol-d4	
13DBD4	1,3-Dichlorobenzene-d4	
DEPD4	Diethyl phthalate-d4	
DNOPD4	Di-n-octyl phthalate-d4	

B. Physical and Chemical Properties

Aldrin: $C_{12}H_8Cl_6$,
 Endrin: $C_{12}H_8Cl_6O$,
 Dieldrin: $C_{12}H_8Cl_6O$,
 Isodrin: $C_{12}H_8Cl_6$,
 DDT: $C_{14}H_9Cl_5$,
 DDE: $C_{14}H_8Cl_4$,
 CPMS: C_7H_7ClS ,
 CPMSO: C_7H_7ClSO ,
 CPMSO2: $C_7H_7ClSO_2$,
 HCCPD: C_5H_6 , mp-10, bp239
 Oxathiane: C_4H_8SO , bp147
 Dithiane: $C_4H_8S_2$, mp110, bp200
 Malathion: $C_{10}H_{19}O_6PS_2$,
 Parathion: $C_{10}H_{14}NO_5PS$,
 Chlordane: mixture
 Supona: $C_{12}H_{14}Cl_3O_4P$,
 DIMP: $C_7H_{17}O_3P$
 Atrazine: $C_8H_{14}ClN_5$,
 Vapona: $C_4H_7Cl_2O_4P$,
 DBCP: $C_3H_5Br_2Cl$,
 DCPD: $C_{10}H_{12}$, mp-1

1066A
14B

C. Chemical Reactions: N/A

III. APPARATUS:

A. Instrumentation:

Hewlett Packard model 5985 (or equivalent) gas chromatograph/mass spectrometer equipped with a fused silica capillary column. The GC/MS is coupled to a Hewlett Packard 1000 computer (or equivalent). The system is operated in the EI Mode and tuned as described in EPA Method 8270.

Packard Becker model 419 (or equivalent) gas chromatograph with a flame-ionization detector coupled to a Hewlett Packard 3390 Integrator is used for GC-screens.

B. Parameters:

1. GC/MS Analysis

Column: 30 m by 0.25 mm (id) DB5 (0.25 um coating) Fused Silica Capillary

Program: 45°C for 4 min then to 280°C at 10°C/min.

Injector Port: 300°C

Electron Energy: 70 ev

Carrier Gas: Helium at about 30 cm/sec

Scanning Range: 35-500

2. GC/FID Screen:

Column: 1.5 m by 2 mm glass

Packing: 1% SP1240DA

Program: 60° for 2 min to 180° at 8°/min

Injection Port: 290°

Detector: 290°

Carrier gas: Nitrogen at about 25 mL/min

3. Injection Volume: 2.0 ul

4. Retention Time (GC/MS): See I-B above.

C. Hardware/Glassware:

1. Soxhlet extractor with water cooled condenser, 500 ml erlenmeyer flask.

2. Kuderna-Danish apparatus with three-ball Snyder column and three ball micro Snyder column.
3. Paper extraction thimble and glass wool to retain sample in Soxhlet extraction device.
4. Teflon boiling chips pre-extracted with methylene chloride.
5. Hot plates - 9" x 10" surface
6. 4L beakers.
7. Micro syringes: 10, 25, 100 and 250 ml.
8. Balance: Analytical, capable of accurately weighing 0.0001 g.
9. Volumetric flasks: 1, 2, 5, 10, 25, 50 and 100 milliliters.

D. Chemicals:

1. Dichloromethane: Burdick and Jackson Pesticide Quality or equivalent.
2. Analytical reference standards or each analyte. Malathion, Parathion, Azodrin, Supona, Vapona, and Atrazine are from EPA (Reference Standards Repository); all others are USATHAMA SARMS or interim SARMS. EPA standards are used only when SARMS are unavailable.
3. Decafluorotriphenylphosphine (DFTPP).
4. d4-1,3,-dichlorobenzene, d4-diethylphthalate, d4-di-n-octylphthalate and d4-2-chlorophenol as surrogates from USATHAMA as SARMS.
5. d10-Phenanthrene as an internal standard.
6. Phenanthrene as GC Screen standard (Chemical).
7. Anhydrous sodium sulfate (dichloromethane rinsed).

IV. STANDARDS:

- A. Stock Solutions: Stock solutions of analytes, phenanthrene, d10-phenanthrene, and surrogates are prepared in 10 mL volumetric flasks at 10.0 mg/mL in dichloromethane and stored at 4°C in the dark. The purity of each analyte must be used to determine the actual final concentration. Since dichloromethane is volatile, care must be taken to monitor potential loss of solvent during storage.
- B. GC/MS Working Standards: The stock analyte and surrogate solutions are combined and diluted in dichloromethane to give 3.75 ug/mL, 7.50 ug/mL, 37.5 ug/mL and 150 ug/mL concentrations of analytes and surrogates. In addition, 50 uL of the d10-phenanthrene internal standard stock solution is added to 10 mL of each final GC/MS working standard.

Preparation	ug/mL conc.		
	Analytes	Surr.	I.S.
1.50 mL each stock, dil. to 100 mL, save 10 mL	150	150	50
25 mL of 625-WS-G, dil. to 100 mL, save 10 mL	37.5	37.5	50
20 mL of 625-WS-E, dil. to 100 mL, save 10 mL	7.50	7.50	50
50 mL of 625-WS-C, dil. to 100 mL, save 10 mL	3.75	3.75	50

- C. Surrogate Spike Standards: The stock surrogate solutions are combined and diluted in dichloromethane to give 150 ug/mL concentrations of each surrogate. An aliquot (1.0 mL) is added to soil samples to give a 10 ug/g spike. Spikes remain on the soil 1 hour before extraction.
- D. GC/MS Internal Standard: The stock solution of d10-phenanthrene (internal standard) is diluted in dichloromethane to give a 2.0 mg/mL solution. A 25 uL aliquot is added to 1.0 mL of final sample extract just prior to GC/MS analysis, yielding the internal standard at 50 ug/mL concentration.
- E. GC Screen Standard: The stock solution of unlabelled phenanthrene is diluted in dichloromethane to give a 15 ug/mL GC Screen Standard.
- F. Certification Standards:
1. The GC/MS must meet all daily calibration checks.

2. For the purpose of certification on standard soil, a series of analyte/surrogate spiking standards are prepared. Dilutions containing all the analyte and surrogate compounds are prepared at concentrations of 3.75, 7.50, 37.5 and 150 ng/ul. Aliquots are added to 15 grams of standard soil and extracted as follows:

SAMPLE	ug/g Spike	ml of Spike ml	Conc. of Spike ug/ml	Final Vol. ml
Control	0.0	None	None	1.0 mL
0.5X	0.25	1.0	3.75	1.0 mL
1.0X	0.50	1.0	7.50	1.0 mL
2.0X	1.00	2.0	7.50	1.0 mL
5.0X	2.50	1.0	37.5	1.0 mL
10X	5.00	2.0	37.5	1.0 mL
20X	10.0	1.0	150	1.0 mL
50X	25.0	2.5	150	10 mL
100X	50.0	5.0	150	10 mL
200X	100	10	150	25 mL

The final volumes noted will keep the analytes and surrogates within the GC/MS working standard concentration range. For the purpose of certification, no GC-FID screens need be employed.

V. PROCEDURES:

A. Quality Assurance:

1. Each soil sample will be spiked with surrogates at the same level.
2. Each sample set will also include a reagent blank to test purity of reagents and cleanliness of glassware.
3. Each sample set will also include a soil method blank spiked with surrogate solution at 10 ug/g.

B. Extraction:

1. Blend 15 g of the solid sample with 30 gm of anhydrous sodium sulfate and place in a paper extraction thimble. The extraction thimble must drain freely for the

duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

2. Place 300 ml of methylene chloride into a 500 ml Erlenmeyer flask containing a boiling stone. The surrogate is spiked onto the soil while it is in the soxhlet extractor. The spike is equilibrated one hour before attaching the flask to the extractor. Extract the solids for 8 hours.
3. Allow the extract to cool after the extraction is complete. Rinse the condensor with the extraction solvent and drain the Soxhlet apparatus into the collecting Erlenmeyer flask. Collect the extract in a 500 ml Kuderna-Danish (K-D) flask fitted with a 10 ml graduated concentrator tube. Wash the extractor flask with 100-125 ml of the extracting solvent.
4. Add 1 clean teflon boiling chip to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 6 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.
5. Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in the GC-FID Screen.
6. If the final volume is to be reduced to 1.0 mls then quantitatively transfer the extract, after GC screen, to a Kuderna Danish apparatus equipped with a graduated ampule. Rinse the volumetric at least three times with 5 mls of methylene chloride. Follow the steps outlined in section V.B.4. except that after cooling remove the graduated ampule, rinsing the Kuderna Danish base and add a fresh boiling chip. Attach a three-ball micro Snyder column and reduce the volume to approximately 0.5 mls. Transfer to a 1.0 ml volumetric flask and wash the ampule twice with 0.2 mls of methylene chloride. Bring the final volume to 1.0 ml and add 25 μ l of the 2.0 mg/ml standard of phenanthrene-d10. Transfer the extract to a 1.0 ml crimp top vial and store in the dark at 4°C.

- C. GC-FID Screening: The sample extracts are analyzed by GC-FID using 2 μ L hand injections (no autosampler) to determine whether the extracts will require either concentration or dilution such that the largest GC-FID peaks will not exceed the highest (150 μ g/mL) GC/MS analyte standards. For example, if there are no GC-FID peaks greater than 15 μ g/mL screen standard, the sample extract can be concentrated to 1.0 mL final volume; this will allow the detection limits to be met while not generating analyte peaks greater than the highest GC/MS standards. The GC-FID attenuation is adjusted so that a 2 μ L injection of the 15 μ g/mL phenanthrene standard gives about 50% full-scale deflection.
- D. GC/MS Calibration: Response factors (RFs) and a standard curve for each analyte and each surrogate are developed via the d10-phenanthrene internal standard by injection of the four GC/MS Standards (3.75 ng/ μ L, 7.5 ng/ μ L, 37.5 ng/ μ L and 150 ng/ μ L). The response factors are updated daily, before the analysis of sample extracts, using the middle (37.5 μ g/mL) standard mix. If the daily calibration RFs differ (using "%D" as defined below) from the average RFs by more than 25% for any of the surrogates then a new standard curve and new set of average response factors must be made. If the daily calibration is within the acceptable "%D" window, then analysis of the sample extracts can proceed.

The percent difference (%D) calculation is $[(\text{daily RF} - \text{average RF}) / \text{average RF}] \times 100$. Calculation and tabulation of daily RFs, average RFs, and "%D" are easily done with Hewlett Packard 1000 or equivalent.

1. Daily GC/MS DFTPP Tune

- a. At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.
- b. The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)
Mass Range: 40 to 450 amu
Maximum Scan Time: 1 sec per scan
- c. Inject a solution containing 50 μ g/mL of DFTPP into the GC/MS system and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

- E. GC/MS: After demonstration of acceptable linearity, the screened extracts are analyzed by GC/MS. Just prior to analysis, 25 μ L of the d10-phenanthrene internal standard is added to 1.0 mL of the sample extract.
- F. Unknown GC/MS Peaks: Unknown GC/MS peaks will be tentatively identified by computer assisted comparison to the NBS 31,000 entry mass spectral library (or equivalent). The mass spectroscopist will use the Hewlett Packard 1000 or equivalent "probability", "confidence" and "class reliability" criteria to assign probabilities of correct structural assignment. Hardcopy mass spectra of all unknowns will be provided with the report. The largest five unknown peaks which are present in excess of ten percent of the area of the m/e 188 peak for d10-phenanthrene internal standard will be library searched.
- G. Qualitative Identification of Target Compounds:
1. Obtain the extracted ion current profile (EICP) for the primary ion listed in Table 2.
 2. The relative retention time between the compound and the internal standard must be within $\pm 3\%$ of the relative retention time obtained in the continuing calibration.
 3. The relative peak heights of the characteristic ions must fall within 20% of the relative intensities of those ions in a reference mass spectra.

VI. CALCULATIONS:

$$A. \text{ ug analyte/mL extract} = \frac{(\text{area of analyte peak})(50 \text{ ug/mL IS})}{(\text{area of I.S.})(\text{analyte RF})}$$

Where I.S. = d-10 phenanthrene internal standard

$$RF = \text{Response factor} = \frac{(\text{area of analyte peak})(50 \text{ ug/mL I.S.})}{(\text{area of I.S.})(\text{conc. of analyte})}$$

$$B. \text{ ug analyte/g sample} = \text{ppm} = \frac{\text{ug analyte/mL extract}}{\text{g sample/mL extract}}$$

C. Results are corrected for recovery and reported on a dry weight basis.

- VII. REFERENCES: Test Methods for Evaluating Solid Waste,
Test Methods 3540 and 8270,
US EPA SW-846, 2nd Edition, July 1982.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass of 442

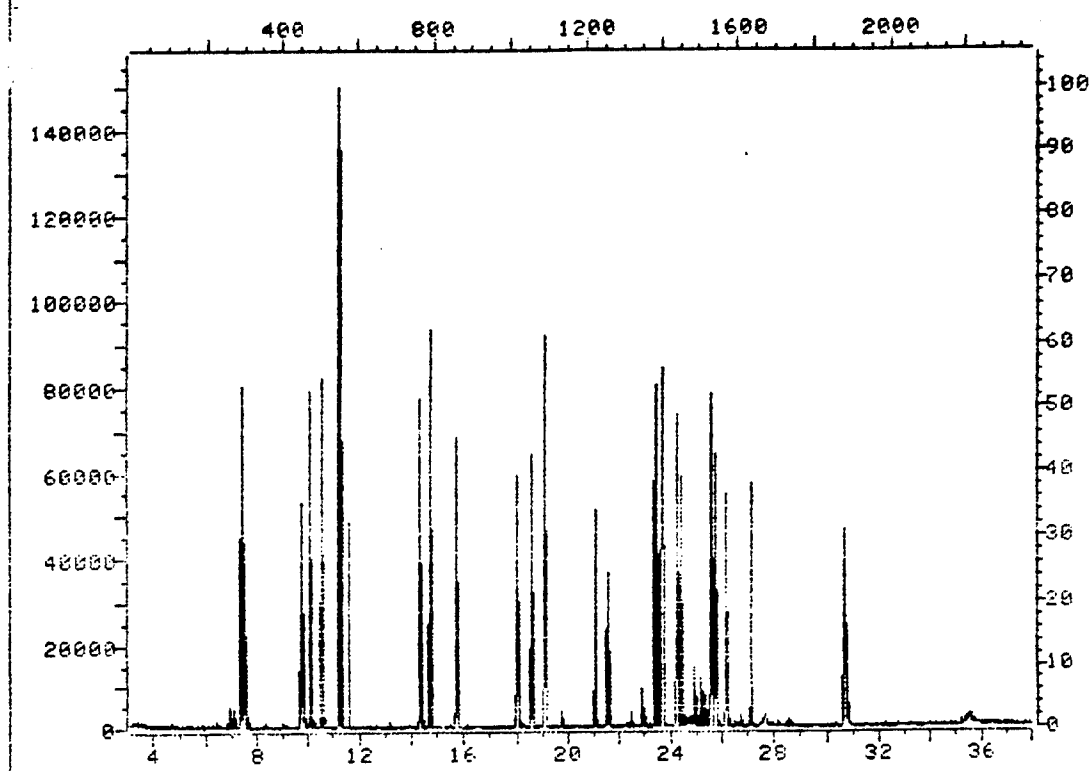
TABLE 2

COMPOUND	ION
Oxathiane	104
DCPD	132
DIMP	123
DMMP	94
Dithiane	120
DBCP	157
Vapona	109
CPMS	158
CL6CP	237
CPMSO	159
CPMSO ₂	175
Atrazine	200
Malathion	173
Aldrin	263
Parathion	291
Isodrin	193
Supona	267
DDE	246
Dieldrin	79
Endrin	263
DDT	235
Chlordane	373
1,3-Dichlorobenzene-d ₄	150
Diethylephthalate-d ₄	153
Di-n-octylphthalate-d ₄	153
Chlorophenol-d ₄	132
Phenanthrene-d ₁₀	188

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14B

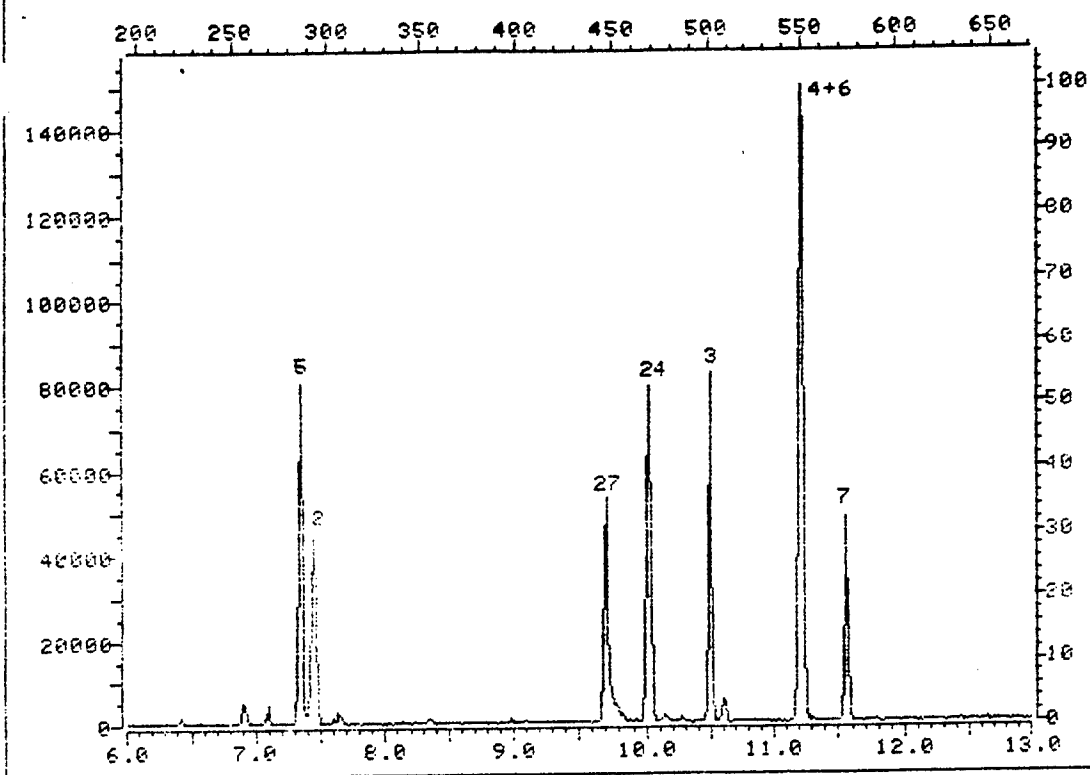
File >AG024 35.0-45.0 amu. 2ul RMA STANDARD D-38 15Ang/ul
TIC



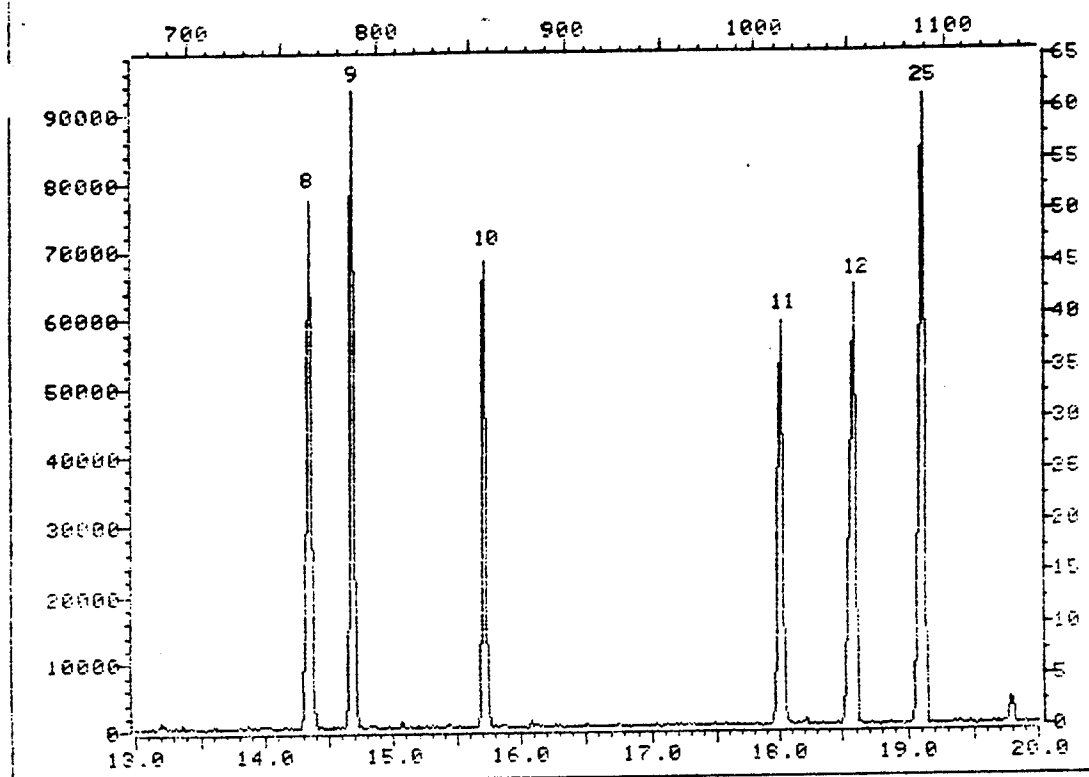
MS data file header from : >AG024

Sample: 2ul RMA STANDARD Operator: CHUCK MS 8/10/85 11:16
Misc : D-38 150ng/ul
Sys. #: 1 MS model: 87 SW/HW rev.: CA ALS # : 0
Method file: HEME01 Tuning file: MTCHW3 No. of extra records: 1
Source temp.: 200 Analyzer temp.: 0 Transfer line temp.: 0

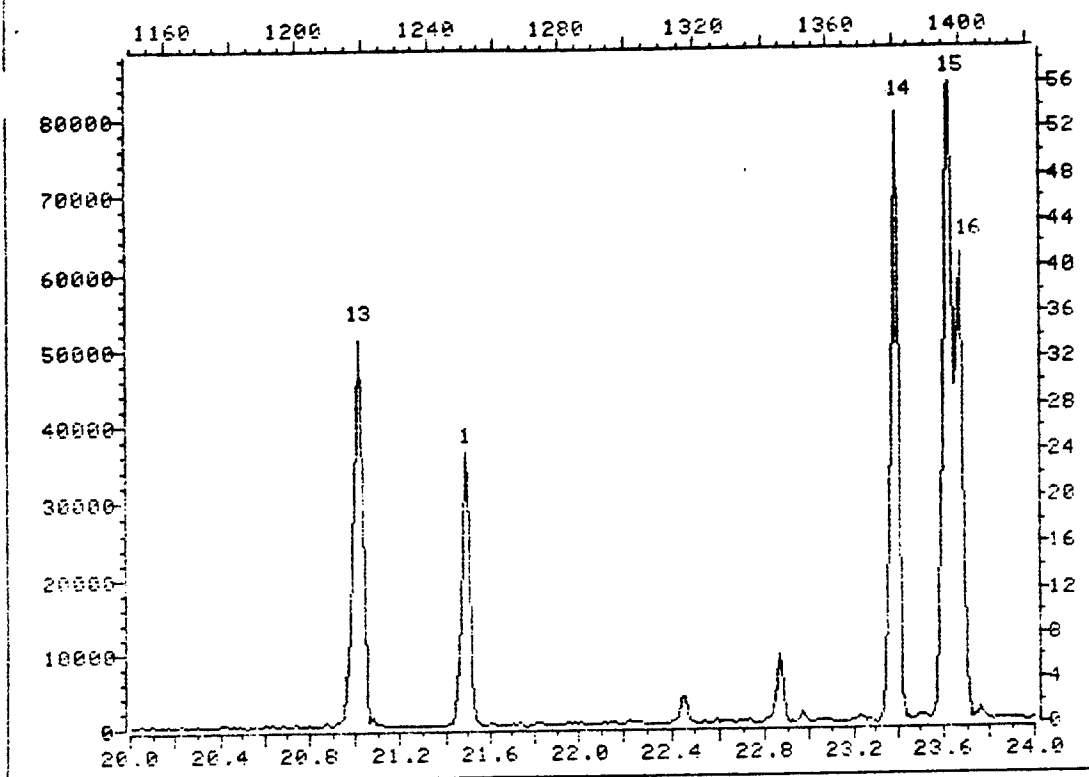
Chromatographic temperatures :	0.	0.	0.	0.	0.
Chromatographic times, min. :	0.0	0.0	0.0	0.0	0.0
Chromatographic rate, deg/min:	0.0	0.0	0.0	0.0	0.0



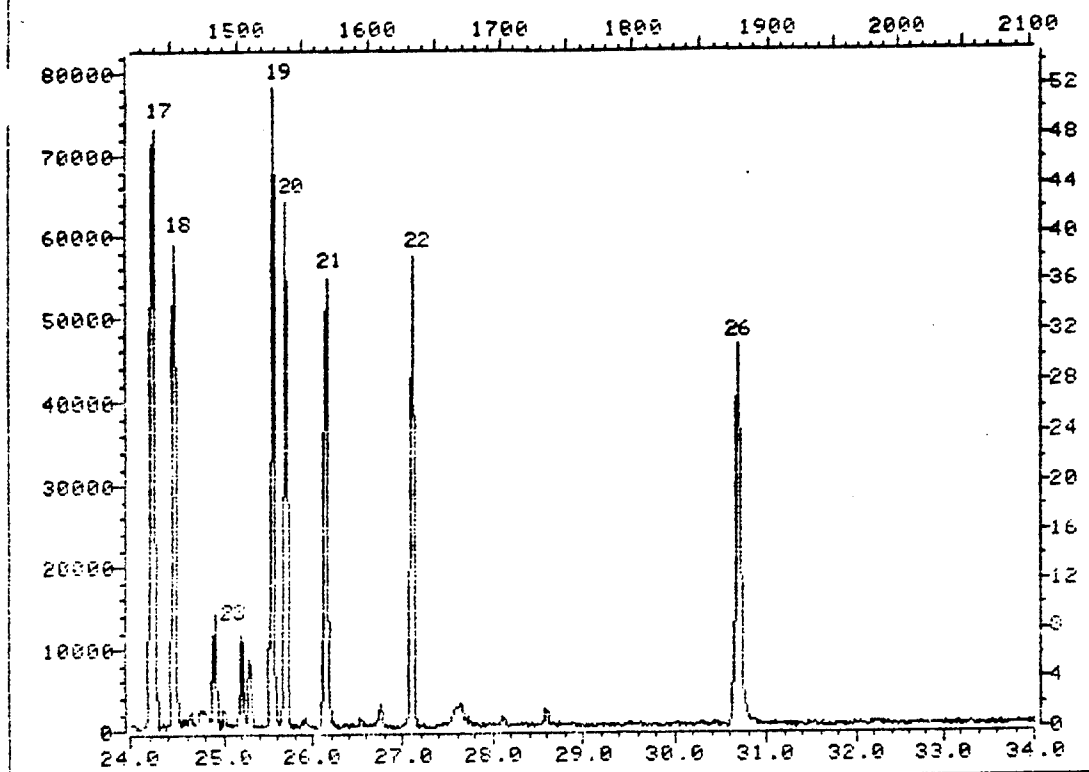
- 2) Oxathiane
- 3) DCPD
- 4) DIMP
- 5) DMMP
- 6) Dithiane
- 7) DBCP
- 24) 1,3-Dichlorobenzene-d4
- 27) Chlorophenol-d4



- 8) Uapona
- 9) CPMS
- 10) HCCPD
- 11) CPMSO
- 12) CPMSO2
- 25) Diethylphthalate-d4



- 1) Phenanthrene-d10
- 13) Atrazine
- 14) Malathion
- 15) Aldrin
- 16) Parathion



- 17) Isodrin
- 18) Supona
- 19) DDE
- 20) Dieldrin
- 21) Endrin
- 22) DDT
- 23) Chlordane (tech)
- 26) Dioctylphthalate-d4

METHOD 3540

SOXHLET EXTRACTION

1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet-extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

2 / WORKUP TECHNIQUES - Organic

5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples:

METHOD 8270

GC/MS METHOD FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- μ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- μ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ($\pm 2^\circ$ C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ± 0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA^a

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

^aJ.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D₁₀-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be used in place of D₁₂-benzo(a)pyrene.

5.9 Column performance standards: D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D₃-phenol, D₈-naphthalene, D₁₀-phenanthrene, D₁₂-chrysene and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D₃-phenol, D₈-naphthalene, D₁₂-chrysene, and D₁₂-benzo(a)pyrene. D₁₂-perylene may be substituted for D₁₂-benzo(a)pyrene. D₁₀-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D₅-phenol or D₃-phenol, D₅-aniline, D₅-nitrobenzene, and D₃-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standards.

C_{is} = Concentration of the internal standard in $\mu\text{g/l}$.

C_s = Concentration of the compound to be measured in $\mu\text{g/l}$.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm 20\%$ of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 $\mu\text{g/ml}$ of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2Cl_2 and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4 , the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- μ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{\text{GPC}(7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

V_s = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{c(7.3.8)}$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within ± 15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within $\pm 20\%$ of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$ = internal standard concentration factor calculated in Section 7.3.8.

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in $\mu\text{g/g}$ without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ($s/R \times 100$) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D₁₀-phenanthrene.

SECTION E

DIBROMOCHLOROPROPANE IN SOILS BY GAS CHROMATOGRAPH/ELECTRON
CAPTURE (GC/EC): USATHAMA CERTIFIED METHOD S9 FOR UBTL;
AND USATHAMA CERTIFIED METHOD Z9 FOR CAL

DEVELOPED BY
MRI, JANUARY 1985

USATHAMA CERTIFIED METHOD S9 FOR UBTL

USATHAMA CERTIFIED METHOD #Z9
Determination of DBCP in Soils and Solids by
Electron Capture Gas Chromatography

(CAL Version 4, 5/21/85)
(USATHAMA Version 1, 5/21/85)

- I. Application: This method is for the quantitative analysis of soil and solid samples for 1,2-dibromo-3-chloropropane.
- A. Tested Concentration Range:
0.005 to 0.10 ug/g.
- B. Sensitivity: The detection limit sample (0.014 ug/g) gave a 8000 height count response. The 0.0025 ug/mL GC working standard gave a 2400 height count response.
- C. Certified Detection Limit: 0.014 ug/g Accuracy: 1.020
- D. Interferences: Electron capture responding compounds with similar retention times.
- E. Analysis Rate: Eight samples can be extracted and analyzed in one day.
- II. Chemistry: DBCP or 1,2-dibromo-3-chloropropane was manufactured at Rocky Mountain Arsenal as Nemagon and Fumazone.
- C3H5Br2Cl
- CAS No.: 96-121-8
M.W.: 236.4
m.p.: 5°C
b.p.: 195°C
- III. Apparatus:
- A. Instrumentation:
1. Varian 3700 gas chromatograph with a ⁶³Ni electron capture detector. Helium carrier and nitrogen makeup gases.
 2. Column: 30 m x 0.25 mm ID DB-5 fused silica capillary column with 25-um film thickness.

3. Integrator: Varian Model Vista 402 data system.

B. Parameters:

1. Column Gas Flow: Helium: 30 cm/sec linear velocity; nitrogen (make-up): 20 mL/min.
2. Temperatures:
Column: 80°C for 2 min, 10°/min to 140°, hold 6 min.
Injection Port: 200°C
Detector: 250°C
3. Injection Volume: 2.0 uL, splitless (open split at 45 sec)
4. Retention Time: 6.3 min.

C. Hardware/Glassware:

1. Glass vial; 40 mL with Teflon-lined cap
2. Volumetric Flasks; 10-mL and 100-mL
3. Volumetric pipets; 1.0-mL, 2.0-mL, 5.0-mL, 10.0-mL, and 20.0-mL
4. Graduated pipets; 0.5-mL
5. Pasteur pipets; (disposable)
6. 8 mL and 15 mL glass test tubes
7. Small glass funnels
8. Separatory funnels, 125 mL
9. Syringes, 50 uL and 10 uL
10. Platform shaker
11. 100 mL amber bottles

D. Chemicals:

1. Hexane, acetone and isooctane (Burdick and Jackson, pesticide grade or equivalent).
2. Sodium sulfate, (analytical reagent, pre-heated to 450°C in a muffle furnace).
3. DBCP SARM Reference Standard

IV. Standards:

A. Standard Solutions:

1. Stock: With a syringe, dilute 100 mg (47.8 uL of liquid DBCP, density 2.09 mg/mL) to 100 mL with acetone in a 100 mL volumetric flask giving 1,000 ug/mL of Stock Standard A.

With a volumetric pipet, dilute 1.0 mL of Stock Standard A with acetone to 100 mL giving 10 ug/mL Stock Standard B.

2. GC: Prepare GC working standards by diluting DBCP standards with the appropriate volumetric or graduated pipets to a final volume of 100 mL with isooctane as follows:

<u>Solution</u>	<u>Volume</u>	<u>Final Conc.</u> <u>(ug/mL)</u>
DBCP-WS-E	0.50 mL of Stock B diluted to 100 mL	0.050
DBCP-WS-D	0.25 mL of Stock B diluted to 100 mL	0.025
DBCP-WS-C	20 mL of WS-E diluted to 100 mL	0.010
DBCP-WS-B	10 mL of WS-E diluted to 100 mL	0.0050
DBCP-WS-A	5 mL of WS-E diluted to 100 mL	0.0025

3. Spiking: Prepare spike standards by diluting DBCP standards with volumetric pipets to a final volume of 100 mL with acetone as follows:

<u>Solution</u>	<u>Volume</u>	<u>Final Conc. (ug/mL)</u>
DBCP-SS-E	10 mL of Stock B diluted to 100 mL	1.00
DBCP-SS-D	5.0 mL of Stock B diluted to 100 mL	0.50
DBCP-SS-C	20 mL of SS-E diluted to 100 mL	0.20
DBCP-SS-B	10 mL of SS-E diluted to 100 mL	0.10
DBCP-SS-A	5 mL of SS-E diluted to 100 mL	0.05
DBCP-SS-MB	100 mL of acetone	0.00

All standards are stored at 4°C in 100 mL amber bottles with Teflon-lined screw caps.

B. Control Spikes:

1. For certification, add 1.0 mL of the following spike standards to 10 g of standard soil, allow it to sit one hour, and then proceed as in part V below:

<u>Designation</u>	<u>Spike Standard</u>	<u>ug/g added to soil</u>
"Method Blank"	DBCP-SS-MB	0.0
0.5X	DBCP-SS-A	0.005
1X	DBCP-SS-B	0.01
2X	DBCP-SS-C	0.02
5X	DBCP-SS-D	0.05
10X	DBCP-SS-E	0.10

2. Daily quality assurance requires the analysis of unspiked standard soil (the "Method Blank"), a spike at 0.020 ug/g, and duplicate spikes at 0.05 ug/g with each batch of samples. These daily spikes are prepared by adding 1.0 mL of spike standards indicated below to 10 g of standard soil, allowing the spikes to sit for one hour, and then proceeding as in V below.

<u>Designation</u>	<u>Spike Standard</u>	<u>ug/g added to soil</u>
MB	DECP-SS-E	0.0
2X	DBCP-SS-C	0.02
5X	DECP-SS-D	0.05
5X dup	DBCP-SS-D	0.05

V. Procedures:

- A. Extraction: A 10 g portion of the soil sample is transferred to a 40 mL vial equipped with a Teflon-lined screw cap. Twenty mL of a 1:1 acetone/hexane solvent mixture is then added to the soil. The vial is capped tightly and shaken in a horizontal position for 4 hr. on a platform shaker. The particulate is allowed to settle. The sample may be centrifuged, if necessary (indicate in the laboratory record book whether centrifugation was required). Ten mL of extract (one-half the total) is removed with a 10 mL pipette and added to a 125 mL separatory funnel containing 50 mL of hexane-rinsed water. The extract is washed with the water by shaking the capped separatory funnel for 15 sec. and the phases are allowed to separate. A few crystals of sodium sulfate speeds phase separation.

The water/acetone solution is drained from the separatory funnel and discarded. The hexane extract is then drained into a 15 mL test tube using a small funnel. The separatory funnel and small transfer funnel are rinsed with enough isooctane to reach to 10 mL calibration mark on the 15 mL test tube, about 0.5 g of sodium sulfate is added, and the sample is thoroughly mixed.

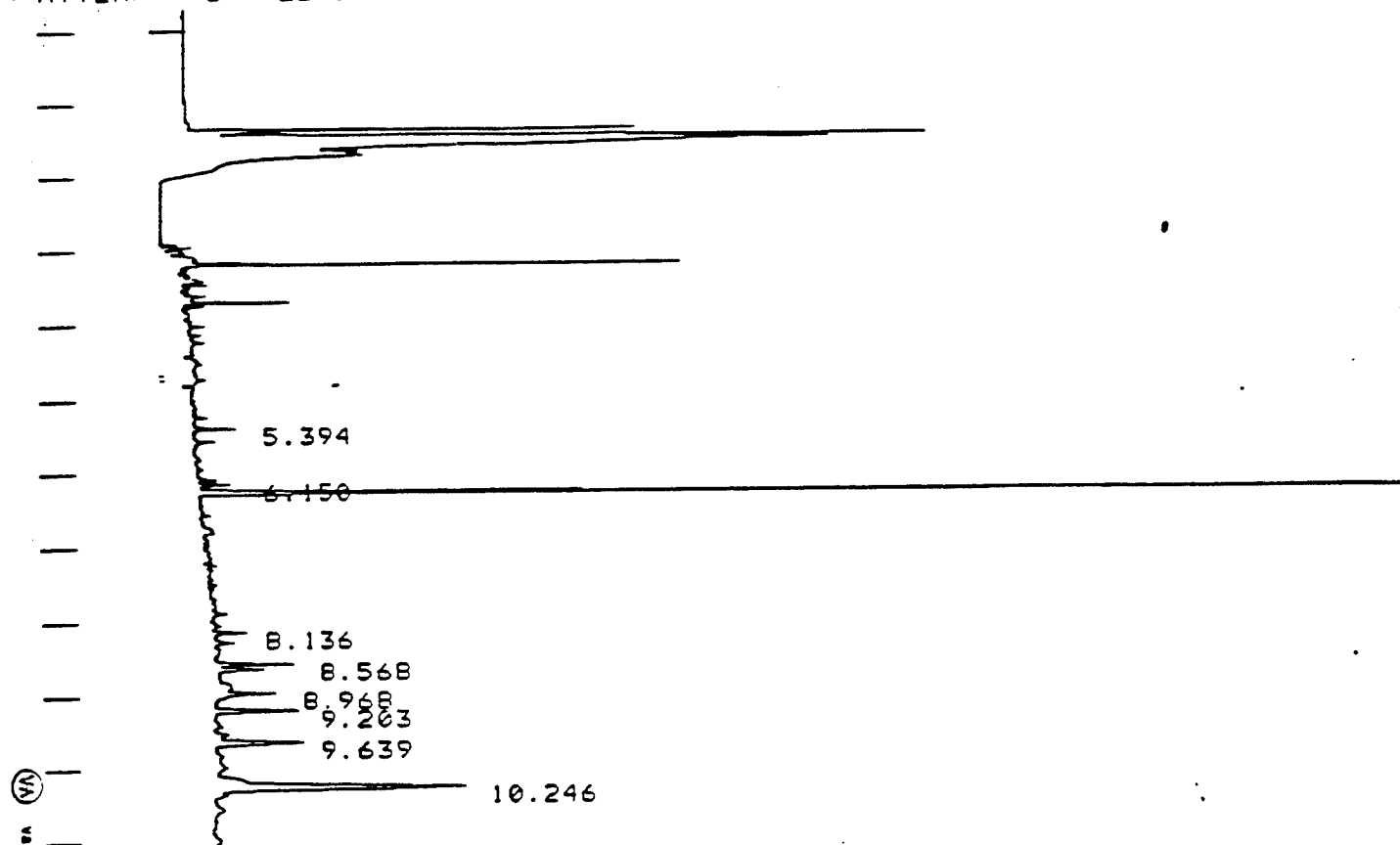
- B. Calibration: Calibrate the GC-EC system using the 0.010 ug/mL working standard solution and prepare a standard curve using the five working standards listed in IV-A-2 above daily prior to sample analysis; responses within the linear range should not exceed $\pm 10\%$ of the average response. Rerun the 0.010 ug/mL working standard after every 10 samples. The run is concluded by reinjecting the standards a second time. Dilute samples whose response is not encompassed by the range of working standard solutions.

- IV. Calculations: Plot the concentration of DBCP versus peak area for each standard. Determine the concentration of analyte in each sample aliquot from the standard curve. The relationship between analyte concentration in the soil sample and in the sample extract is as follows:

$$\text{Conc in Soil (ug/g)} = \frac{\text{Conc in Extract (ug/mL)} \times \text{Final Volume (mL)} \times 2}{\text{Original Sample Weight (g)}}$$

Report results on a dry soil weight basis and correct for percent recovery (based on certification data).

CHART SPEED 1.0 CM/MIN
ATTEN: 8 ZERO: 5% 1 MIN/TICK



(V)

varian / sunnyvale calif. p/n 03-906362-00

TITLE: DBCP

15:29 9 MAR 85

CHANNEL NO: 4

SAMPLE: 0.010UG/ML

METHOD: DBCP

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	HEIGHT COUNTS	SEP CODE
1		0.0000	5.394	272	EV
2		0.0000	5.572	140	VB
3		0.0000	6.150	203	BV
4	DBCP	0.0109	6.270	9149	VB
5		0.0000	8.136	214	BB
6		0.0000	8.568	503	BV
7		0.0000	8.636	307	VB
8		0.0000	8.968	338	BB
9		0.0000	9.203	554	BB
10		0.0000	9.639	564	BB
11		0.0000	10.246	1550	BB

TOTALS: 0.0109 13800

DIVISOR: 1.00000

MULTIPLIER: 1.00000

NOTES:

30M X .25MM 1D DB-5

80/2/10/140/6

SPLITLESS THEN OPEN AT 45SEC

CERTIFICATION RESULTS - CAL LAB - *PCBP* - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.030833333333 SD= 0.0356817657326

FOUND CONC
MEAN= 0.0295416666667 SD= 0.0366416004571

N0. RUNS 4 TOTAL X-Y ALL RUNS 24 N0. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= -0.00190850882186
SLOPE= 1.02000569152

USE FOR ACCURACY
R= 0.993286419717

MEAN SQR DEV OF POINTS FROM REGRESSION= 1.878356056E-5
ST ERROR EST= 0.00433400052641

USE FOR PRECISION
T FOR CONFIDENCE BAND

D.F. = 22

TWO TAIL P LEVEL IS .1

t= 1.71713909197

X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S)

y(c)= 0.00580449011294

x(d)= 0.0150386804951

RECEIVED

MAY 02 1985

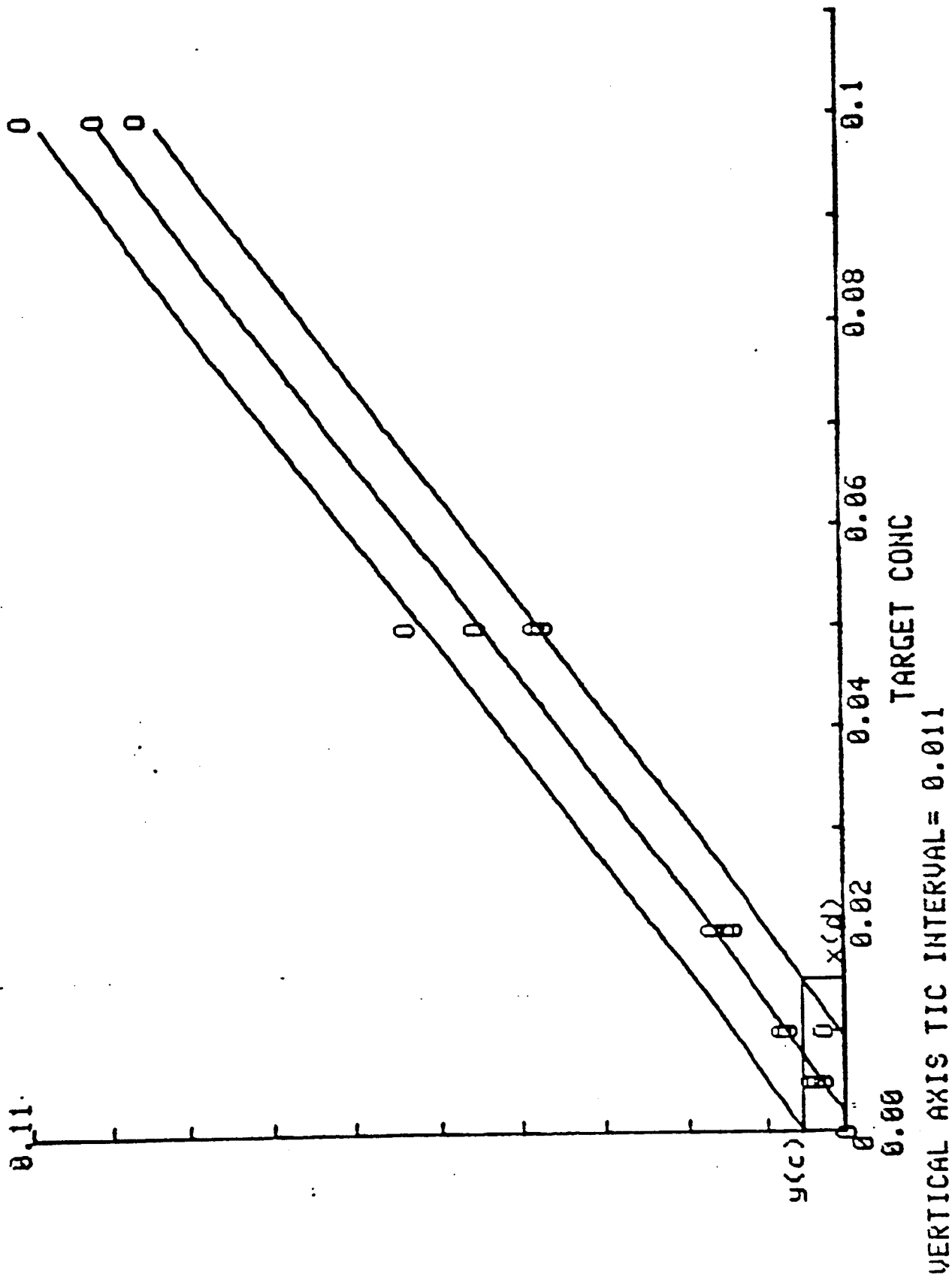
CERTIFICATION RESULTS - CAL LAB - *PCBP* - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC.

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.005	0.004	0.005	0.003	0.004
0.010	0.009	0.009	0.003	0.008
0.020	0.019	0.016	0.016	0.017
0.050	0.059	0.042	0.041	0.050
0.100	0.094	0.100	0.100	0.110

CERTIFICATION RESULTS - CAL LAB - ~~QDBP~~ - 5-1-85
 RUNS 1 2 3 4
 FOUND CONC



CERTIFICATION RESULTS - CAL LAB - ~~QAPP~~ - 5-1-85

RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.005	0.004	0.001	-20.000	20.412
0.010	0.007	0.003	-27.500	39.618
0.020	0.017	0.001	-15.000	8.319
0.050	0.048	0.008	-4.000	17.430
0.100	0.101	0.007	1.000	6.568
Means		0.003	-13.100	18.469

MAY 02 1985

CERTIFICATION RESULTS - CAL LAB - *QCBP* - 5-1-85

RUNS 5 6 7 8

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.005	0.004	0.005	0.003	0.004
0.010	0.009	0.009	0.003	0.008
0.020	0.019	0.016	0.016	0.017
0.050	0.059	0.042	0.041	0.058

CERTIFICATION RESULTS - CAL LAB - ~~DOBP~~ - 5-1-85
RUNS 5 6 7 8
ANALYSIS OF 20 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.017 SD= 0.0182381901226

FOUND CONC
MEAN= 0.01525 SD= 0.0181191233667

N0. RUNS 4 TOTAL X-Y ALL RUNS 20 N0. CONCENTR 20
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= -0.0012792721519
SLOPE= 0.972310126582

USE FOR ACCURACY

R= 0.978699498193

MEAN SQR DEV OF POINTS FROM REGRESSION= 1.46057929E-5
ST ERROR EST= 0.00382175259499

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 18

TWO TAIL P LEVEL IS .1

t= 1.73406096408

X(0) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C

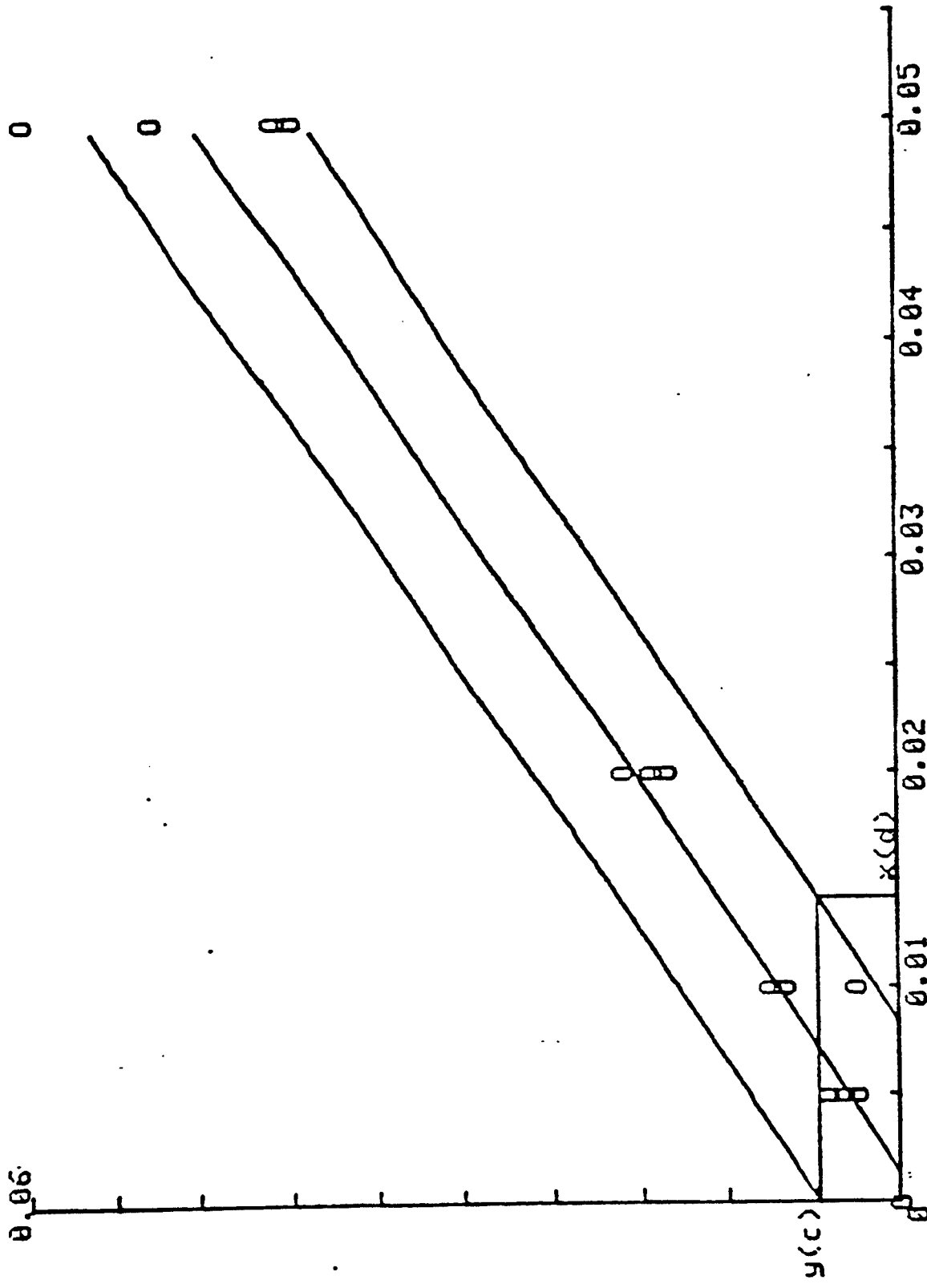
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

Y(C)= 0.00565783305033

X(d)= 0.0141232198036

CERTIFICATION RESULTS - CAL LAB - ~~QCBP~~ - 5-1-85
 RUNS 5 6 7 8
 FOUND CONC



TARGET CONC
 VERTICAL AXIS TIC INTERVAL= 0.0059

CERTIFICATION RESULTS - CAL LAB - ~~DOBP~~ - 5-1-85

RUNS 5 6 7 8

STATISTICAL DATA USED TO DETERMINE PERCENT
INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.005	0.004	0.001	-20.000	20.412
0.010	0.007	0.003	-27.500	39.618
0.020	0.017	0.001	-15.000	8.319
0.050	0.048	0.008	-4.000	17.430
Means		0.003	-16.625	21.445

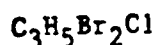
USATHAMA CERTIFIED METHOD Z9 FOR CAL

ANALYSIS OF DIBROMOCHLOROPROPANE (DBCP) IN SOILS BY GC/EC

1. APPLICATION: This method is applicable for the quantitative analysis of dibromochloropropane (DBCP) in soil samples.

- a. Tested Concentration Range: 0.005 to 0.10 µg/g.
- b. Sensitivity: 25 pg gave a detector response of 23% full-scale deflection at an attenuation of 32 with a range of 10.
- c. Certified Detection Limit: ~~0.007~~ ^{0.005 µg/g} µg/g
Certified Upper Concentration Limit: 0.1 µg/g
- d. Interferences: Electron capture responding compounds with similar retention times.
- e. Analysis Rate: 10 samples can be extracted and analyzed in 2 days.

2. CHEMISTRY: DBCP or 1,2,-dibromo-3-chloropropane was manufactured at Rocky Mountain Arsenal as Nemagon and Fumazone.



CAS No.: 96-121-8
M.W.: 236.4
m.p.: 5°C
b.p.: 196°C

3. APPARATUS:

- a. Instrumentation:

- (1) Varian 6000 gas chromatograph with a ^{63}Ni electron capture detector. Helium carrier and nitrogen make-up gas.
- (2) Column: 30 m x 0.25 mm ID DB-5 fused silica capillary column with 0.25-µm film thickness
- (3) Integrator: The integration was performed by a Hewlett Packard 3557 Laboratory Automation System.

- b. Parameters:

- (1) Gas Flows:
Helium: 30 cm/sec linear velocity (flow control set at 2 mL/min)

- (2) Temperatures:
Column: 80°C for 2 min, then 10°C/min to 140°C
Injection Port: 200°C
Detector: 250°C
- (3) Injection Volume: 1.0 µL, splitless (open split at 45 sec)
- (4) Retention Time: 6.37 min

c. Hardware/Glassware:

- (1) 40 mL amber glass VOA vial with Teflon-lined screw cap.
- (2) Volumetric Flask; 10-mL and 100-mL
- (3) Syringes: 1.0 mL, 100 µL, 250 µL, 25 µL
- (4) Pasteur pipets (disposable)
- (5) 2-mL and 4-mL amber vials with Teflon-lined screw caps
- (6) Small glass funnels
- (7) Separatory funnels, 125-mL
- (8) Syringes, 50-µL and 10-µL
- (9) Aluminum foil
- (10) Stainless steel spatulas
- (11) Kraft Rotator
- (12) 40-mL amber bottles

d. Chemicals:

- (1) Hexane (Burdick and Jackson, pesticide grade)
- (2) Acetone distilled-in-glass (Burdick and Jackson)
- (3) Sodium sulfate, analytical reagent, pre-heated to 450°C in a muffle furnace
- (4) DBCP (PA 722, Lot 2118)

4. STANDARDS:

a. Calibration Standards

- (1) Stock: With a syringe, dilute 25 mg (12.0 µL of liquid DBCP, density 2.09 g/mL) to 25 mL with acetone in a 25-mL volumetric flask giving 1,000 µg/mL of Stock Standard A.

With a syringe, dilute 100 μ L of Stock Standard A with acetone to 10 mL in a volumetric flask to prepare 10 μ g/mL Stock Standard B.

- (2) Working Standards: Prepare working standards by diluting DBCP standards with the appropriate volumetric or graduated pipet to a final volume of 100 mL with hexane as follows:

<u>Solution</u>	<u>Volume</u>	<u>Final Conc.</u> (μ g/mL)
10X-W	50 μ L of Stock B diluted to 10 mL with hexane	0.050
5X-W	25 μ L of Stock B diluted to 10 mL with hexane	0.025
2X-W	200 μ L of 10X-W diluted to 1 mL with hexane	0.010
1X-W	100 μ L of 10X-W diluted to 1 mL with hexane	0.0050
0.5X-W	50 μ L of 10X-W diluted to 1 mL with hexane	0.0025

b. Control Spikes:

- (1) Spike Stocks: Prepare spike stocks by diluting DBCP standards with volumetric pipets to a final volume of 100 mL with acetone as follows:

<u>Solution</u>	<u>Volume</u>	<u>Final Conc.</u> (μ g/mL)
10X-S	10 mL of Stock B diluted to 100 mL with acetone	1.00
5X-S	5.0 mL of Stock B diluted to 100 mL with acetone	0.50
2X-S	20 mL of 10X-S diluted to 100 mL with acetone	0.20
1X-S	10 mL of 10X-S diluted to 100 mL with acetone	0.10
0.5X-S	5 mL of 10X-S diluted to 100 mL with acetone	0.50

All standards are stored at 0°C in amber bottles with Teflon-lined screw caps.

- (2) **Certification Samples:** Prepare spiked samples by adding 1.0 mL of the appropriate control spike stock solution to 10 g of standard background soil with a volumetric pipet. Mix and allow to equilibrate for 1 hr. Analyze by the procedure given in the following section. The resulting soil spike levels are:

<u>Level</u>	<u>Spike Solution</u>	<u>Final Conc.</u> <u>($\mu\text{g/g}$)</u>
Blank	--	0.000
0.5X	0.5X	0.005
1X	1X	0.010
2X	2X	0.020
5X	5X	0.050
10X	10X	0.100

- (3) **Daily Control Samples:** Four quality control samples are to be included with each lot of field samples. They are the blank (unspiked soil), one 1X level spike ($0.01 \mu\text{g/g}$) and two 5X level spikes ($0.05 \mu\text{g/g}$). They are prepared in the same manner as the certification samples by adding 1.0 mL of the indicated control spike stock solution to 10 g of standard background soil with a volumetric pipet. The sample is mixed and allowed to equilibrate for one hour. The control samples are analyzed with the field samples according to the procedure given in the following section.

<u>Level</u>	<u>Spike Solution</u>	<u>Final Conc.</u> <u>($\mu\text{g/g}$)</u>
Blank	--	0.000
1X	1X	0.010
5X	5X	0.050
5X	5X	0.050

5. PROCEDURE:

- a. **Sample Handling:** Soil core sections received from the field in polybutyrate tube sections will be subsampled in the laboratory using a stainless steel coring tube inserted lengthwise into the end of the core section. This procedure will allow a composite subsample of the entire core length to be taken for analysis.

The core subsample will be taken from the center of the core section to avoid analyzing soil which has contacted the polybutyrate tube walls. Subsampling using the coring device will be repeated until sufficient quantity of soil is removed to perform all the required analyses.

The center core samples will be transferred to the dull side of clean aluminum foil, the sample thoroughly mixed using a clean

stainless steel spatula, and the entire subsample transferred to a clean amber glass container with Teflon-lined lid for storage prior to removal of aliquots for analysis.

For surface soil samples, the entire contents of the sample bottle will be transferred to the dull side of clean aluminum foil. The sample is returned to the original sample bottle or to a clean amber glass container for storage prior to removal of aliquots for analysis.

- b. Extraction: Samples are to be extracted within 7 days of sample collection. A 10-g portion of the soil sample is transferred to a 40-mL amber glass VOA vial equipped with a Teflon-lined screw cap. Twenty (20) milliliters of a 1:1 acetone/hexane solvent mixture are then added to the soil with a volumetric pipet. The centrifuge tube is capped tightly and shaken for 4 hrs. on a shaker. The particulate is allowed to settle. The sample may be centrifuged, if necessary (indicate in the laboratory record book whether centrifugation was required). Ten milliliters of extract (one-half the total) is removed with a 10-mL volumetric pipette and added to a 125-mL separatory funnel containing 50 mL of hexane-extracted water. The extract is washed with the water by shaking the capped separatory funnel for 15 sec. The phases are allowed to separate for 10 min. A few crystals of sodium sulfate speeds phase separation.

The water/acetone solution is drained from the separatory funnel and discarded. The hexane extract is then drained into a 10-mL volumetric flask using a small funnel. The separatory funnel and small transfer funnel are rinsed with enough hexane to reach the mark on the 10-mL volumetric flask, and the sample is thoroughly mixed. A small quantity of sodium sulfate is then added as a drying agent.

- c. Extract handling: Using a disposable pipet, a portion of the 10-mL hexane extract is transferred to a 2-mL amber glass GC autosampler vial with a Teflon-lined cap for GC/ECD analysis. The remainder of the extract is transferred to a 4-mL amber glass vial with a Teflon-lined cap as a backup sample. Samples are stored at 0°C until analysis. Samples are to be analyzed within 30 days of sample extraction.
- d. Calibration: Make replicate 1.0- μ L injections of 5X-W until the response is reproducible (\pm 5-10% response variation). Prepare a daily calibration curve prior to sample analysis by injecting standards and measuring detector response. Also, rerun the 5X-W standard at intervals of ten samples to demonstrate continuing reproducibility (\pm 5-10%). The run is concluded by reinjecting the standards a second time. Dilute samples whose response is not encompassed by the range of standards.

6. CALCULATIONS: Plot the concentration of DBCP versus peak area for each standard. Determine the concentration of analyte in each sample aliquot from the standard curve. The standard curve is a linear regression fit to the equation $y = mx + b$. The square of the correlation efficient ranged from 0.993 to 0.999. The relationship between analyte concentration in the soil sample and in the sample extract is as follows:

$$\text{Conc. in Soil } (\mu\text{g/g}) = \text{Conc. in Extract } (\mu\text{g/mL}) \times 2$$

$$\text{where } \frac{10 \text{ mL Extract}}{10 \text{ g Soil}} \times 2 \text{ (one-half of extract)} = 2$$

Report results on a dry soil weight basis, corrected for recovery as determined during certification.

7. REFERENCE: ESE Technical Proposal for Litigation and Technical Support and Services, Rocky Mountain Arsenal, November 1984.

CERTIFICATION RESULTS - UBTL - DBCP - 5-1-85
 RUNS 5 6 7 8

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.005	0.005	0.005	0.004	0.004
0.010	0.009	0.010	0.010	0.010
0.020	0.018	0.020	0.018	0.021
0.050	0.046	0.046	0.046	0.046

CERTIFICATION RESULTS -- UBTL - DBCP - 5-1-85
RUNS 5 6 7 8
ANALYSIS OF 20 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.017 SD= 0.0182381901226

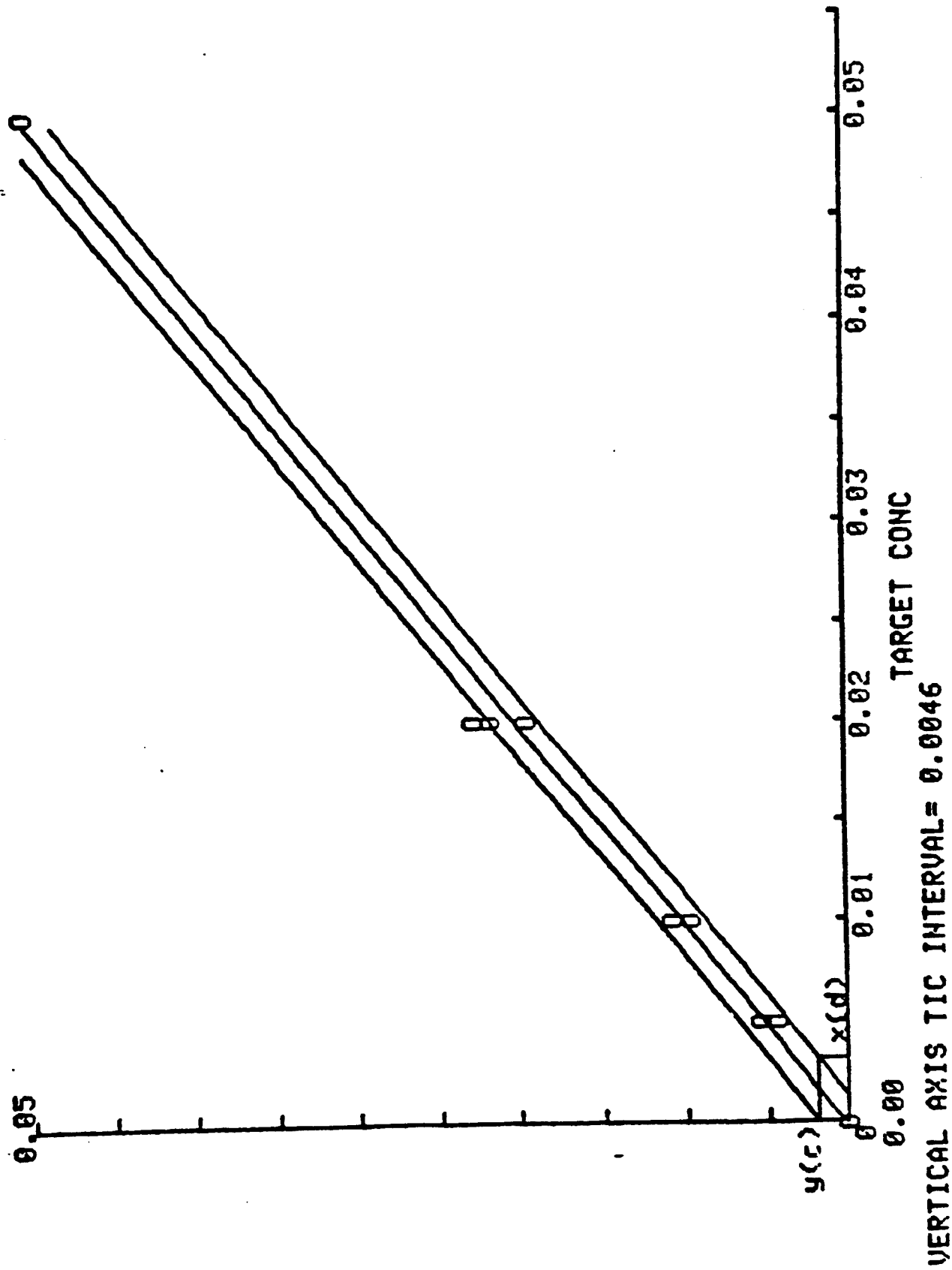
FOUND CONC
MEAN= 0.0159 SD= 0.0167956761353

N0. RUNS 4 TOTAL X-Y ALL RUNS 20 N0. CONCENTR 20
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 2.610759494E-4
SLOPE= 0.919936708861
USE FOR ACCURACY
R= 0.998946422983
MEAN SQR DEV OF POINTS FROM REGRESSION= 6.271097046E-7
ST ERROR EST= 7.919025853E-4
USE FOR PRECISION
T FOR CONFIDENCE BAND

D.F.= 18
TWO TAIL P LEVEL IS .1
t= 1.73406096408
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE
MEASURED 1 TIME(S))
y(c)= 0.00169850849053
x(d)= 0.00311417918565

CERTIFICATION RESULTS -- UBTL -- DBCP -- 5-1-85
 RUNS 5 6 7 8
 FOUND CONC



CERTIFICATION RESULTS - UBTL - DBCP - 5-1-85

RUNS 5 6 7 8

STATISTICAL DATA USED TO DETERMINE PERCENT

INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.005	0.005	0.001	-10.000	12.830
0.010	0.010	0.001	-2.500	5.128
0.020	0.019	0.002	-3.750	7.792
0.050	0.046	0.000	-8.000	0.000
Means			-6.063	6.439

CERTIFICATION RESULTS - UBTL - DBCP - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.005	0.005	0.005	0.004	0.004
0.010	0.009	0.010	0.010	0.010
0.020	0.018	0.020	0.018	0.021
0.050	0.046	0.046	0.046	0.046
0.100	0.089	0.098	0.098	0.093

CERTIFICATION RESULTS -- UBTL -- DBCP -- 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.030833333333 SD= 0.0356817657326

FOUND CONC
MEAN= 0.029 SD= 0.0336284041432

N0. RUNS 4 TOTAL X-Y ALL RUNS 24 N0. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= -1.87820148E-5
SLOPE= 0.941149686966
USE FOR ACCURACY
R= 0.998616601212
MEAN SQR DEV OF POINTS FROM REGRESSION= 3.268846691E-6
ST ERROR EST= 0.00180799521325

USE FOR PRECISION
T FOR CONFIDENCE BAND

D.F.= 22

TWO TAIL P LEVEL IS .1

t= 1.71713909197

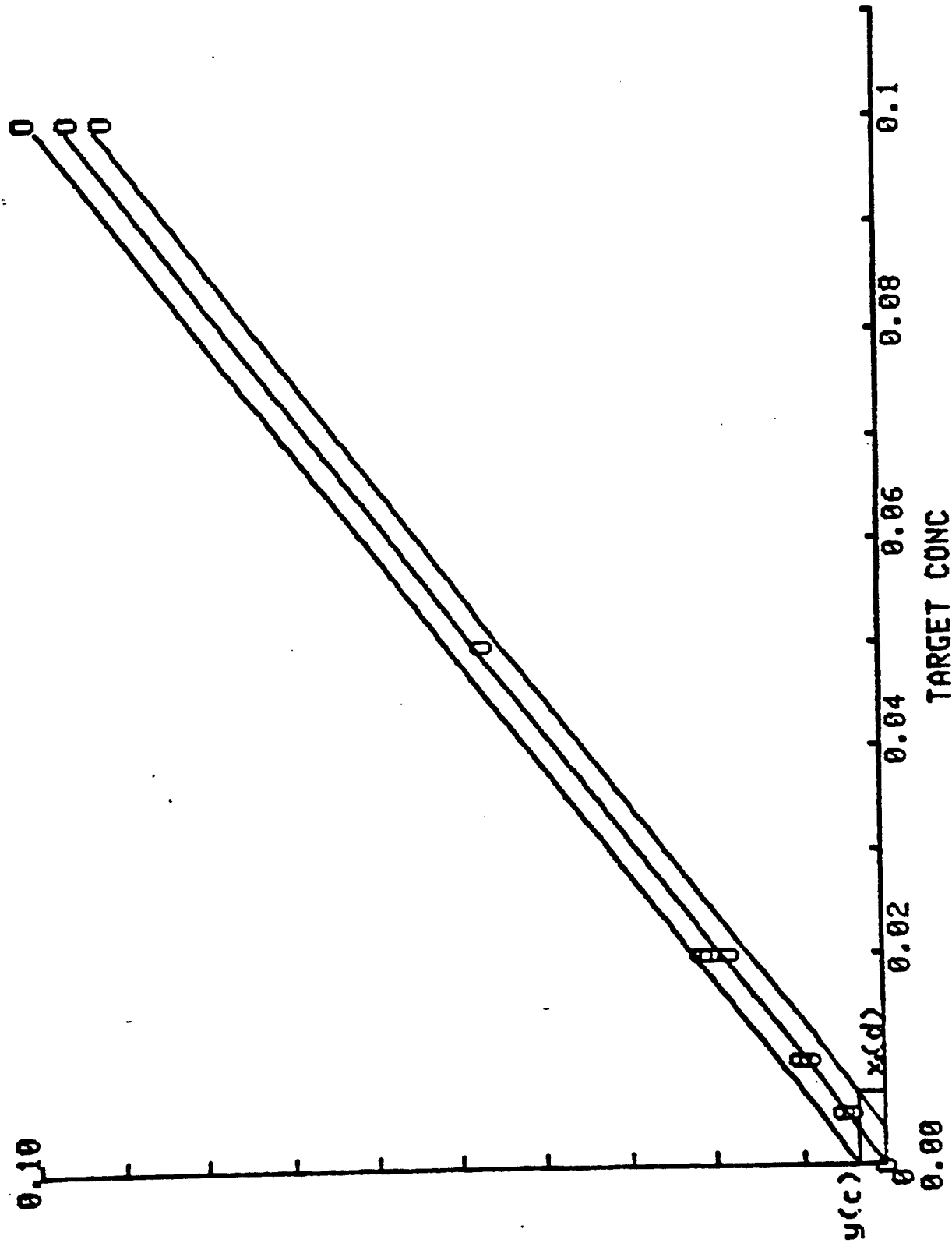
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

y(c)= 0.00319881453808

x(d)= 0.00681720571788

CERTIFICATION RESULTS -- UBTL -- DBCP -- 5-1-85
 RUNS 1 2 3 4
 FOUND CONC



VERTICAL AXIS TIC INTERVAL= 0.0098

CERTIFICATION RESULTS - UBTL - DBCP - 5-1-85

RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT INACCURACY AND IMPRECISION

Nn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.005	0.005	0.001	-10.000	12.830
0.010	0.010	0.001	-2.500	5.128
0.020	0.019	0.002	-3.750	7.792
0.050	0.046	0.000	-8.000	0.000
0.100	0.095	0.004	-5.500	4.613
Means		0.001	-5.950	6.073

CERTIFICATION RESULTS DBCP BY GC/EC - UBTL - 3/27/85

DBCP BY GC/EC

TARGET CONC. VS FOUND CONC

Helium Carrier Gas

Target Conc UG/G	Found Conc UG/G
0.000	0.000
0.005	0.006
0.010	0.012
0.025	0.022
0.050	0.046
0.100	0.095

CERTIFICATION RESULTS DBCP BY GC/EC - UBTL - 3/27/85
DBCP BY GC/EC
ANALYSIS OF 6 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.031666666667 SD= 0.0380350715349

FOUND CONC
MEAN= 0.030166666667 SD= 0.0356225583959

N0. RUNS 1 TOTAL X-Y ALL RUNS 6 N0. CONCENTR 6
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 5.357142857E-4

SLOPE= 0.935714285714

USE FOR ACCURACY

R= 0.99908488791

MEAN SQR DEV OF POINTS FROM REGRESSION= 2.901785714E-6

ST ERROR EST= 0.00170346285967

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 4

TWO TAIL P LEVEL IS .1

t= 2.13183865604

X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C

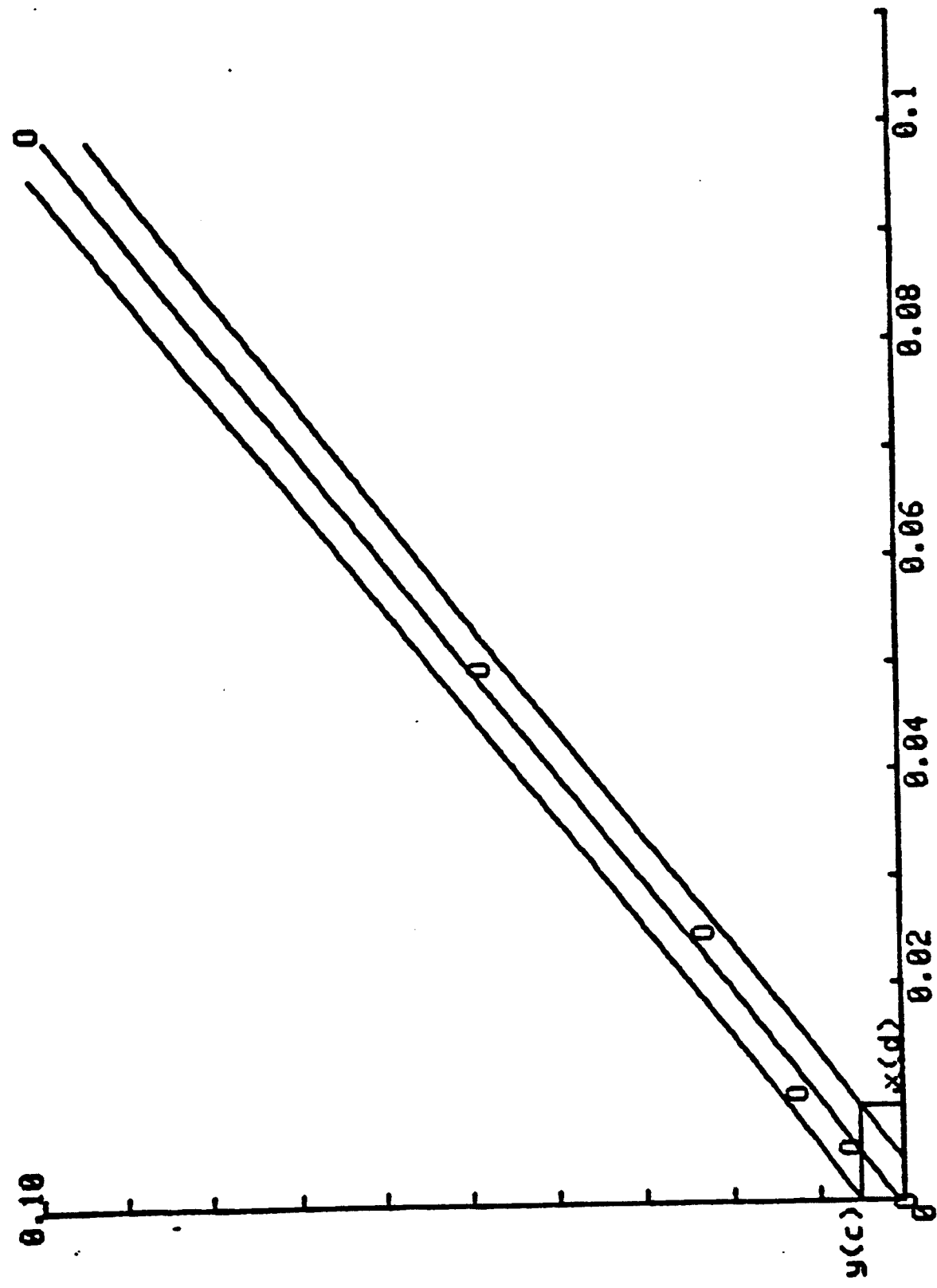
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

y(c)= 0.00468470147988

x(d)= 0.00875442688093

CERTIFICATION RESULTS DBCP BY GC/EC - UBTL - 3/27/85
DBCP BY GC/EC
FOUND CONC



TARGET CONC

VERTICAL AXIS TIC INTERVAL= 0.0095

CERTIFICATION RESULTS DBCP BY GC/EC - UBTL - 3/27/83

DBCP BY GC/EC

STATISTICAL DATA USED TO DETERMINE PERCENT

INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.005	0.006	0.000	20.000	0.000
0.010	0.012	0.000	20.000	0.000
0.025	0.022	0.000	-12.000	0.000
0.050	0.046	0.000	-8.000	0.000
0.100	0.095	0.000	-5.000	0.000
Means			3.000	

SECTION F

METALS IN SOIL AND SOLID SAMPLES BY INDUCTIVELY COUPLED
ARGON PLASMA SPECTROSCOPY: USATHAMA CERTIFIED METHOD P9 FOR UBTL;
AND USATHAMA CERTIFIED METHOD ____ FOR CAL

DEVELOPED FROM
USATHAMA METHOD 7S

USATHAMA CERTIFIED METHOD P9 FOR UBTL

**METALS IN SOIL AND SOLID SAMPLES
BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY**

1. APPLICATION

This method is applicable to the analysis of the following elements in soils and solid samples:

<u>Element</u>	<u>Chemical Symbol</u>
Cadmium	Cd
Chromium	Cr
Copper	Cu
Lead	Pb
Zinc	Zn

A. TESTED CONCENTRATION RANGES

The tested concentration ranges in standard soil are:

<u>Analyte</u>	<u>Tested Spike Concentration Range (ug/g)</u>	<u>Wavelength</u>	<u>Confirmation Wavelength</u>
Cadmium	0.25 to 50	228.802	214.438
Chromium	2.5 to 500	205.552	267.716
Copper	2.5 to 500	324.754	327.396
Lead	2.5 to 500	220.353	216.999
Zinc	2.5 to 500	213.856	206.200
Aluminum	—	308.215	396.152
Iron	—	259.940	238.204

Aluminum and iron are determined in order to perform interelement corrections.

B. SENSITIVITY

The sensitivity of a spectral line is a measure of the rate of change of emission intensity with concentration of analyte. Listed below are the background corrected intensities, expressed as counts, for the analytes at their detection limits:

<u>Element</u>	<u>Intensity (counts)</u>
Cd	1700
Cr	1700
Cu	1200
Pb	2000
Zn	2300

C. DETECTION LIMITS

The detection limits in standard soil, calculated according to Hubaux and Vos, are:

<u>Analyte</u>	<u>Certified Detection Limit ($\mu\text{g/g}$)</u>	<u>Range ($\mu\text{g/g}$)</u>
Cd	0.74	0.74 - 50
Cr	6.5	6.5 - 500
Cu	4.7	4.7 - 500
Pb	8.4	8.4 - 500
Zn	8.7	8.7 - 500

D. INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference for an element that could occur

in a sample but for which there is no channel in the instrument array. (Please refer to attached table). These data are intended for use only as a rudimentary guide for indicating potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferences can be assumed.

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by diluting the sample and/or utilizing standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the top of the nebulizer. This affects aerosol flow rate, causing instrumental drift. Wetting the argon prior to nebulization, the use of a top washer, or sample dilution have been used to control this problem. Also, the use of a high solid nebulizer can reduce salt build-up in the nebulizer and can also prevent drifting and loss of sensitivity in the instrument. In addition, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with ICP technique; however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

Because of the differences between various makes and models of satisfactory instruments, no detailed universal operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument.

In order to correct for interferences in the RMA standard soil matrix the Perkin Elmer ICP 6500 was programmed to use the interelement correction for aluminum and iron. It should be noted that this correction as programmed in the ICP 6500 corrects the intensities of all elements in the analyte list for both aluminum and iron.

An interference check sample is used to verify that the correction routines are functioning properly. The interference check sample is prepared to approximate the background found in the standard soil. Regardless of the means used to achieve correction for interferences the analyte readings obtained for the interference check sample must be within $\pm 20\%$ of the expected value.

The interference check sample is prepared by adding the indicated volumes of 1000 $\mu\text{g/mL}$ (ppm) standard solutions to a 100 mL volumetric flask and diluting to volume with 1% (volume/volume) nitric acid.

<u>Element</u>	<u>mL of 1000 µg/mL SARM</u>	<u>Final Concentration in 100 mL (µg/mL)</u>
Cd	0.010	0.1
Cr	0.10	1.0
Cu	0.10	1.0
Pb	0.10	1.0
Zn	0.10	1.0
Al	20	200
Ca	25	250
Fe	25	250
Mg	10	100

E. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 50 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day by one technician.

2. CHEMISTRY

- A. Alternate nomenclature and Chemical Abstract Service (CAS) registry number.

<u>Analyte</u>	<u>Alternate Nomenclature</u>	<u>CAS Registry Number</u>
Cd	--	7440-43-9
Cr	--	7440-47-3
Cu	--	7440-50-8
Pb	--	7439-92-1
Zn	--	7440-66-6
Al	--	7429-90-5
Fe	--	7439-89-6

B. PHYSICAL AND CHEMICAL PROPERTIES OF ANALYTES

<u>Analyte</u>	<u>Melting Point (°C)</u>	<u>Boiling Point (°C)</u>	<u>Density (g/mL at 20°C)</u>
Cd	320.9	765	8.65
Cr	1875	2665	7.19
Cu	1083	2595	8.96
Pb	327.4	1725	11.4
Zn	419.5	906	7.14

C. CHEMICAL REACTIONS

None.

3. APPARATUSA. INSTRUMENTATION

Perkin-Elmer ICP 6500 sequential inductively coupled argon plasma emission spectrometer equipped with software for background correction and inter-element correction.

B. INSTRUMENT OPERATING PARAMETERS

The instrument settings are as follows:

Incident RF power	1.1 Kilowatts (KW)
Observation height	14 mm
Sample argon flow rate	0.96 L/min
Coolant argon flow rate	12 L/min

C. HARDWARE/GLASSWARE

1. Pyrex® Phillips beakers, 125 mL, with watch glasses.
2. Hot plate.
3. Oxford macro-pipetter (with disposable tips).
4. Disposable beakers (10-mL capacity).
5. Whatman 11cm #2 filter paper.
6. Volumetric Flasks, 1000 mL, 50 mL.
7. Filter funnels.

D. CHEMICALS AND REAGENTS

1. Ultrex (or equivalent) concentrated nitric acid (HNO_3) and Ultrex (or equivalent) hydrochloric acid (HCl).
2. 1,000 $\mu\text{g/mL}$ (ppm) Reference Standard Solutions. (SARM's)
3. A 1,000 $\mu\text{g/mL}$ (ppm) Fisher Reference Standard Solution of aluminum was substituted for the 1,000 $\mu\text{g/mL}$ Baker SARM which was found to contain 0.5 $\mu\text{g/mL}$ copper.
4. Millipore Super Q deionized distilled water (or equivalent).

4. STANDARDSA. CALIBRATION STANDARDS (to calibrate instrument only)

1. Obtain the 1000 µg/mL reference standard solution for each metal.
2. Prepare the dilute multi-element stock calibration standard (Standard C-1) by pipetting 10 mL of each reference standard solution (1 mL of the cadmium solution) into a 1,000-mL volumetric flask and diluting to volume with 1.0% (volume/volume) nitric acid.
3. Subsequent calibration standards are prepared according to the following table. Dilutions are made with 1% nitric acid. Calibration standard C-1 is also shown for completeness.

<u>Calibration Standard</u>	<u>Volume (mL) of C-1</u>	<u>Final Volume (mL)</u>	<u>Final Concentration (µg/mL) for Cadmium</u>	<u>Final Concentration (µg/mL) for Other Metals</u>
C-1	--	--	1	10
C-2	20	100	0.2	2
C-3	10	100	0.1	1
C-4	5	100	0.05	0.5
C-5	2	100	0.02	0.2
C-6	1	100	0.01	0.1
C-7	0.5	100	0.005	0.05
C-8 (Blank)	0	100	0	0

4. Initial calibration is verified using all eight calibration standards.
5. Daily calibration is verified using C-1, C-2, C-4, C-7, and C-8.
6. Calibration standard C-2 is analyzed at a frequency of 10%. The purpose of this check is to determine instrument drift. If agreement is not within $\pm 10\%$ of the expected value, the analysis must be terminated, until the problem is identified and corrected. The instrument is then recalibrated before continuing the analysis.
7. Special high range calibration standards were made for aluminum and iron to allow for interelement correction.

B. CONTROL SPIKES

1. The recovery of each metal must be tested through the complete sample work-up, which includes the digestion. To facilitate this process, two sets of multi-metal dilute standard solutions are prepared. These solutions are prepared from the 1000 $\mu\text{g/mL}$ (ppm) reference standard solutions of each metal. Solution A1 is prepared by pipetting 25 mL of the 1000 $\mu\text{g/mL}$ (ppm) reference standard solutions of copper, chromium, and zinc, and 2.5 mL of the 1000 $\mu\text{g/mL}$ (ppm) cadmium solution into a 250 mL volumetric flask and diluting to volume. Solution A2 is prepared by pipetting 25 mL of the 1000 $\mu\text{g/mL}$ (ppm) lead solution into another 250 mL volumetric flask and diluting to volume. Solution B is prepared by pipetting 25 mL each of Solutions A1 and A2 into a 500 mL volumetric flask and diluting to volume. Dilutions are made using 1% nitric acid.
2. To prepare working spike solutions, spike aliquots of the dilute standard solutions into 100 mL volumetric flasks according to the following table, and dilute to volume with 1% nitric acid.

Spike Level	Volume of Dilute Standard Solution (mL)	Concentration in Working Spike Solutions	
		Cadmium $\mu\text{g/mL}$	Other Metals $\mu\text{g/mL}$
0	0	0	0
0.5x	5.0 (B)	.025	.250
1x	10.0 (B)	.050	.50
2x	20.0 (B)	.100	1.0
5x	50.0 (B)	.250	2.5
10x	100.0 (B)	.500	5.0
20x	10.0 each A1 & A2	1.00	10.0
50x	25.0 each A1 & A2	2.50	25.0
100x	*	—	—

*Follow Special Instructions: Do not mix equal volumes of solutions A1 and A2 together without dilution, as complex metal precipitations may occur upon standing. To prepare the 100x control spike sample, spike separate 5 mL aliquots of A1 and A2 into a single 1 gram standard soil sample.

3. Spike 10 mL of each working spike solution into separate 1 gram samples of standard soil, except as noted in 4.B.2 for the 100X spike. The spiked samples are allowed to stand for at least one hour before proceeding with digestion. The resultant specific concentration levels for each metal are as follows:

Control Spike Concentration Levels (ug/g)

<u>Analyte</u>	<u>0.5x</u>	<u>1x</u>	<u>2x</u>	<u>5x</u>	<u>10x</u>	<u>20x</u>	<u>50x</u>	<u>100x</u>
Cd	0.25	0.5	1.0	2.5	5.0	10	25	50
Cr	2.5	5	10	25	50	100	250	500
Cu	2.5	5	10	25	50	100	250	500
Pb	2.5	5	10	25	50	100	250	500
Zn	2.5	5	10	25	50	100	250	500

4. Analyze a complete set of spiked samples, including a reagent blank (unspiked soil), on four successive days for quantitative certification.
5. For daily quality control analyze a set of three spiked samples (two at the high level and one at the low level) and a reagent blank (unspiked soil) with each lot. One gram of soil is spiked with a total of 10 mL of the required spiking solution/solutions (5 mL each of solutions D1 and D2). A 10 mL aliquot of 1% nitric acid is added to the reagent blank (unspiked soil) sample. The spiked samples are allowed to stand for at least one hour before proceeding with digestion.

The high level spiking solutions are prepared by adding the indicated volumes of 1000 ug/mL (ppm) SARM solutions to separate 500 mL volumetric flasks and diluting each to volume with 1% nitric acid.

High Level Daily QC Spiking Solutions

<u>Analyte</u>	<u>Volume of 1000 µg/mL SARM Added to 500 mL Vol. Flask</u>	<u>Conc. (µg/mL) in High Level Spiking Soln.</u>	<u>Amount (µg) spiked Onto Soil in a 5 mL Aliquot</u>
Solution D1			
Cd	2.5	5	25
Cr	10	20	100
Cu	10	20	100
Zn	25	50	250
Solution D2			
Pb	25	50	250

The low level spiking solution is prepared by adding the indicated volumes of 1000 µg/mL (ppm) SARM solution to a 500 mL volumetric flask and diluting to volume with 1% nitric acid.

Low Level Daily QC Spiking Solution

<u>Analyte</u>	<u>Volume of 1000 µg/mL SARM Added to 500 mL Vol. Flask</u>	<u>Conc. (µg/mL) in Low Level Spiking Soln.</u>	<u>Amount (µg) spiked Onto Soil in a 10 mL Aliquot</u>
Cd	0.125	0.25	2.5
Cr	0.50	1.0	10
Cu	0.50	1.0	10
Pb	1.25	2.5	25
Zn	2.50	5.0	50

5. PROCEDUREA. SAMPLE PREPARATION

1. Weigh 1.0-gram soil samples and quantitatively transfer to 125-mL Phillips beakers.
2. Add 3.0 mL of concentrated nitric acid; cover the beakers with watch glasses, place on a hot plate, evaporate to near dryness, and cool. It is important that this digestion stay on the wet side of near dryness, that is, no area on the bottom of the Phillips beaker should become dry.
3. Repeat Step 2 until the digestion is complete.

4. Add 2.0 mL of 1+1 HNO₃ and 2.0 mL of 1+1 HCl to the residue, and heat for five minutes. Note the presence and appearance of any remaining residue.
5. Wash down the sides of the beakers and the watch glass covers with deionized water.
6. Filter the samples through nitric acid rinsed Whatman 11 cm #2 filter paper.
7. Dilute each sample to a final volume of 50.0 mL with deionized water.

B. CALIBRATION AND ANALYSIS

The procedures for sequential analysis described in the manufacturer's operator's manual call for calibration using calibration standard C-1 only. Linearity is verified by analyzing the set of liquid standards as if they were samples. The correlation coefficient of the linear regression fit must be 0.996 or better.

6. CALCULATIONS

- A. The spectrometer provides direct readout of solution concentrations.
- B. Determine the concentration of metal in soil/sediment matrix (on a dry-weight basis) according to the following formula:

$$\text{Concentration (}\mu\text{g/g)} = \frac{\mu\text{g/L metal} \times V_e}{W_d}$$

where: W_d = dry weight of sample in extract (in grams)

V_e = volume of extract (in liters)

7. REFERENCES

EPA Method 200.7, EPA 600/4-79-020, Revised March 1983.

8. DATA



Test Method

Inductively Coupled Plasma— Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes—Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects. (See 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be

added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the

determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved — Those elements which will pass through a 0.45 μm membrane filter.

3.2 Suspended — Those elements which are retained by a 0.45 μm membrane filter.

3.3 Total — The concentration determined on an unfiltered sample following vigorous digestion (9.3), or the sum of the dissolved plus suspended concentrations (9.1 plus 9.2.)

3.4 Total recoverable — The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (9.4).

3.5 Instrumental detection limit — The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity — The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 Instrument check standard — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 Interference check sample — A solution containing both interfering and analyte elements of known concentration that can be used to

verify background and interelement correction factors. (See 7.6.2)

3.9 Quality control sample — A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 Calibration standards — A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 Linear dynamic range — The concentration range over which the analytical curve remains linear.

3.12 Reagent blank — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 Calibration blank — A volume of deionized, distilled water acidified with HNO_3 and HCl . (See 7.5.1)

3.14 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined, however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (14.7, 14.8 and 14.9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as 1) overlap of a spectral line from another element; 2)

unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

The interference information, which was collected at the Ames Laboratory,¹ is expressed at analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the

¹Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow-rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 Serial dilution—If the analyte concentration is sufficiently high (min-

imally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 % of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

5.2.2 Spike addition—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect. **Caution.** The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See 5.2.3).

5.2.3 Comparison with alternate method of analysis—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 Wavelength scanning of analyte line region—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 Operating conditions — Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the

responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp gr 1.06).

7.1.2 Hydrochloric acid, conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 Nitric acid, conc. (sp gr 1.41).

7.1.5 Nitric acid, (1+1): Add 500 mL conc. HNO₃ (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution, stock, 1 mL = 100 µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 Antimony solution stock, 1 mL = 100 µg Sb: Dissolve 0.2669 g K(SbO)C₄H₄O₆ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 Arsenic solution, stock, 1 mL = 100 µg As. Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.4 Barium solution, stock, 1 mL = 100 µg Ba. Dissolve 0.1516 g BaCl_2 (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 Beryllium solution, stock, 1 mL = 100 µg Be. Do not dry. Dissolve 1.966 g $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.6 Boron solution, stock, 1 mL = 100 µg B. Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 Cadmium solution, stock, 1 mL = 100 µg Cd. Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.8 Calcium solution, stock, 1 mL = 100 µg Ca. Suspend 0.2498 g CaCO_3 dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.9 Chromium solution, stock, 1 mL = 100 µg Cr. Dissolve 0.1923 g of Cr_2O_3 in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.10 Cobalt solution, stock, 1 mL = 100 µg Co. Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3 . Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 Copper solution, stock, 1 mL = 100 µg Cu. Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.12 Iron solution, stock, 1 mL = 100 µg Fe. Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3 . Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with deionized, distilled water.

7.3.13 Lead solution, stock, 1 mL = 100 µg Pb. Dissolve 0.1599 g $\text{Pb}(\text{NO}_3)_2$ in minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.14 Magnesium solution, stock, 1 mL = 100 µg Mg. Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.15 Manganese solution, stock, 1 mL = 100 µg Mn. Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.16 Molybdenum solution, stock, 1 mL = 100 µg Mo. Dissolve 0.2043 g $(\text{NH}_4)_2\text{MoO}_4$ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 Nickel solution, stock, 1 mL = 100 µg Ni. Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3 , cool and dilute to 1,000 mL with deionized, distilled water.

7.3.18 Potassium solution, stock, 1 mL = 100 µg K. Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water dilute to 1,000 mL.

7.3.19 Selenium solution, stock, 1 mL = 100 µg Se. Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 Silica solution, stock, 1 mL = 100 µg SiO_2 . Do not dry. Dissolve 0.4730 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.21 Silver solution, stock, 1 mL = 100 µg Ag. Dissolve 0.1575 g AgNO_3 in 100 mL of deionized, distilled water and 10 mL conc. HNO_3 . Dilute to 1,000 mL with deionized, distilled water.

7.3.22 Sodium solution, stock, 1 mL = 100 µg Na. Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.23 Thallium solution, stock, 1 mL = 100 µg Tl. Dissolve 0.1303 g TlNO_3 in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.24 Vanadium solution, stock, 1 mL = 100 µg V. Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.3.25 Zinc solution, stock, 1 mL = 100 µg Zn. Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.

7.4 Mixed calibration standard solutions—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5) Add 2 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability. (See 7.6.3.) Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 Mixed standard solution I—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 Mixed standard solution II—Barium, copper, iron, vanadium, and cobalt.

7.4.3 Mixed standard solution III—Molybdenum, silica, arsenic, and selenium.

7.4.4 Mixed standard solution IV—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 Mixed standard solution V—Antimony, boron, magnesium, silver, and thallium.

NOTE 1. If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3 13) is used in establishing the analytical curve while the reagent blank (3 12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1-1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3 7), an interference check sample (3 8) and a quality control sample (3 9) are also required for the analyses.

7.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1)

7.6.2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest by known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 $\mu\text{g/L}$ or 5 times the estimated

detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2)

7.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3)

8. Sample handling and preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order. (See Notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCH-ROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through

an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45- μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45- μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferable at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3 . Cover the

beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane.

Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3 . Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended".

NOTE 4 In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3 . Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3 . Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could

clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total".

NOTE 5 If low determinations of boron are critical, quartz glassware should be used.

NOTE 6 If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

10. Procedure

10.1 Set up instrument with proper operating parameters established in 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 $\mu\text{g/L}$ extended flush times of 1 to 2 min. may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a

sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that method of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_x , are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s . To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated.

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x , and thus c_s is much greater than c_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.

3 The interference effect must be constant over the working range of concern.

4 The signal must be corrected for any additive interference

11. Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within $\pm 5\%$ of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of two standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration

standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within $\pm 5\%$ of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

Precision and Accuracy

13.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

References

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Table 1. Recommended Wavelengths and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, $\mu\text{g/L}^2$
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see ³
Selenium	196.026	75
Silica (SiO ₂)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

¹The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1.)

²The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

³Highly dependent on operating conditions and plasma position

Table 2. Analyte Concentration Equivalents (mg/L) Arising From Interferents at the 100 mg/L Level

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
		—	—	—	—	—	—	0.21	—	—	1.4
Aluminum	308 215	—	—	—	—	0.08	—	—	—	.25	0.45
Antimony	206 833	0.47	—	2.9	—	—	—	—	—	—	1.1
Arsenic	193 696	1.3	—	0.44	—	—	—	—	—	—	—
Barium	455 403	—	—	—	—	—	—	—	—	0.04	0.05
Beryllium	313 042	—	—	—	—	0.32	—	—	—	—	—
Boron	249 773	0.04	—	—	—	—	—	—	—	—	—
Cadmium	226 502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317 933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267 716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228 616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324 754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259 940	—	—	—	—	—	—	0.12	—	—	—
Lead	220 353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279 079	—	0.02	0.11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257 610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202 030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231 604	—	—	—	—	—	—	—	—	—	—
Selenium	196 026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288 158	—	—	0.07	—	—	—	—	—	0.08	0.01
Sodium	588 995	—	—	—	—	—	—	—	—	—	—
Thallium	190 864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292 402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213 856	—	—	—	0.14	—	—	—	0.29	—	—

Table 3. Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Ti	10		
V	1		
Zn	10		

Table 4. ICP Precision and Accuracy Data

Element	Sample #1			Sample #2			Sample #3		
	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD	True Value µg/L	Mean Reported Value µg/L	Mean Percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories

USATHAMA CERTIFIED METHOD __ FOR CAL

METALS IN SOIL AND SOLID SAMPLES
BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY

1. APPLICATION

This method is applicable to the analysis of the following elements in soils and solid samples:

<u>Element</u>	<u>Chemical Symbol</u>
Cadmium	Cd
Chromium	Cr
Copper	Cu
Lead	Pb
Boron	B
Arsenic	As
Aluminum	Al
Zinc	Zn

A. TESTED CONCENTRATION RANGES

The tested concentration ranges in standard soil are:

<u>Analyte</u>	<u>Tested Spike Concentration Range (ppm)</u>
Cadmium	2.5 to 500
Chromium	2.5 to 500
Copper	2.5 to 500
Lead	2.5 to 500
Boron	2.5 to 500
Arsenic	2.5 50 to 5000
Aluminum	2.5 to 500
Zinc	2.5 to 500

B. SENSITIVITY

The sensitivity of a spectral line is a measure of the rate of change of emission intensity with concentration of analyte.

Listed below are the intensities, expressed as counts, for the analytes at their detection limits:

<u>Element</u>	<u>Intensity (counts)</u>
Cd	(To be completed during certification.)
Cr	
Cu	
Pb	
B	
As	
Al	
Zn	

C. DETECTION LIMITS

The detection limits in standard soil, calculated according to Hubaux and Vos, are:

<u>Analyte</u>	<u>Concentration</u> <u>(ug/g)</u>
Cd	(To be completed during certification)
Cr	
Cu	
Pb	
B	
As	
Al	
Zn	

D. INTERFERENCES

Broadly defined, an interference is any unwanted radiation that reaches the photomultiplier tubes. It can arise from background continuum or as true spectral interferences. Sources of background continuum are black-body radiation, bremsstrahlung radiation, and recombination phenomena. These are compensated for by "spectrum shifting," i.e., measuring emission intensity on both sides of each analytical line. The average radiation detected "off-center" is subtracted from the intensity measurement taken at the analytical line. Spectral interferences occur when the wavelength separation of the emission lines is less than the spectral bandpass of the detector. By determining the ratio of affecting element to affected element, the computer is programmed to compensate for the unwanted radiation. Iron, for example, will give rise to a false signal for cadmium, as will aluminum and calcium for lead. These corrections are relatively small when compared with the interference due to unwanted background. No major interferences were encountered during documentation of this method.

E. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 50 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day by one technician.

2. CHEMISTRY

A. Alternate nomenclature and Chemical Abstract Service (CAS) registry number.

<u>Analyte</u>	<u>Alternate Nomenclature</u>	<u>CAS Registry Number</u>
Cd	--	(To be completed during certification.)
Cr	--	
Cu	--	
Pb	--	
B	--	
As	--	
Al	--	
Zn	--	

B. PHYSICAL AND CHEMICAL PROPERTIES OF ANALYTES

<u>Analyte</u>	<u>Melting Point (°C)</u>	<u>Boiling Point (°C)</u>	<u>Density (g/mL at 20°C)</u>
Cd	(To be completed during certification.)		
Cr			
Cu			
Pb			
B			
As			
Al			
Zn			

C. CHEMICAL REACTIONS

None.

3. APPARATUS

A. INSTRUMENTATION

Perkin-Elmer ICP 6500 sequential inductively coupled argon plasma emission spectrometer equipped with software for background correction and inter-element correction.

B. INSTRUMENT OPERATING PARAMETERS

The instrument settings are as follows:

Incident RF power 1.8 Kilowatts (KW)
Observation height
Sample argon flow rate
Coolant argon flow rate

C. HARDWARE/GLASSWARE

1. Pyrex® Phillips beakers, 125 mL, with watch glasses.
2. Hot plate.
3. Oxford macro-pipetter (with disposable tips).
4. Disposable beakers (10-mL capacity).
5. Gelman 42-mm glass-fiber filter pads.
6. Volumetric Flasks, 1000 mL, 50 mL.

D. CHEMICALS AND REAGENTS

1. Reagent-grade concentrated nitric acid (HNO_3) and hydrochloric acid (HCl).
2. 1,000-ppm Reference Standard Solutions.

4. STANDARDS

A. CALIBRATION STANDARDS (to calibrate instrument only)

1. Obtain the 1000-ppm reference standard solution for each metal.
2. Prepare the dilute multi-element stock calibration standard (Standard C-1) by pipetting 10 mL of each reference standard solution (100 mL of the arsenic solution) into a 1,000-mL volumetric flask and diluting to volume with 1.0% (volume/volume) nitric acid.

3. Subsequent calibration standards are prepared according to the following table. Dilutions are made with 1% nitric acid. Calibration standard C-1 is also shown for completeness.

<u>Calibration Standard</u>	<u>Volume (mL) of C-1</u>	<u>Final Volume (mL)</u>	<u>Final Concentration (µg/mL) for Arsenic</u>	<u>Final Concentration (µg/mL) for Other Metals</u>
C-1	--	--	100	10
C-2	20	100	20	2
C-3	10	100	10	1
C-4	5	100	5	0.5
C-5	2	100	2	0.2
C-6	1	100	1	0.1
C-7	0.5	100	0.5	0.05
C-8 (Blank)	0	100	0	0

4. Initial calibration is accomplished using all eight calibration standards.
5. Daily calibration is accomplished using C-1, C-2, C-4, C-7, and C-8.

B. CONTROL SPIKES

1. The recovery of each metal must be tested through the complete sample workup, which includes the digestion. To facilitate this process, two multi-metal working spike solutions are prepared. These solutions are prepared from the 1000-ppm reference standard solutions of each metal. Solution A is prepared by pipetting 50 mL of the 1000-ppm reference standard solution of each metal (500 mL of the arsenic solution) into a 1000 mL volumetric flask and diluting to volume. Solution B is prepared by pipetting 100 mL of Solution A into a 1000 mL volumetric flask and diluting to volume. Dilutions are made using 1% nitric acid.
2. Spike the following amounts of the working spike solution into 1 gram of standard soil. All of the spiked samples

are prepared at once by the simple volume additions shown in the following table.

<u>Spike Level</u>	<u>Volume of Working Spike Solution (mL)</u>	<u>Amount of Arsenic Spiked (ug)</u>	<u>Amount of Other Metals Spiked (ug)</u>	<u>Final Volume After Digestion mL</u>
0	0	0	0	50.0
0.5x	0.5 (B)	25	2.5	50.0
1x	1.0 (B)	50	5.0	50.0
2x	2.0 (B)	100	10.0	50.0
5x	5.0 (B)	250	25.0	50.0
10x	10.0 (B)	500	50	50.0
20x	2.0 (A)	1000	100	50.0
50x	5.0 (A)	2500	250	50.0
100x	10.0 (A)	5000	500	50.0

3. The resultant specific concentration levels for each metal are as follows:

Control Spike Concentration Levels (ug/g)

<u>Analyte</u>	<u>0.5x</u>	<u>1x</u>	<u>2x</u>	<u>5x</u>	<u>10x</u>	<u>20x</u>	<u>50x</u>	<u>100x</u>
Cd	2.5	5	10	25	50	100	250	500
Cr	2.5	5	10	25	50	100	250	500
Cu	2.5	5	10	25	50	100	250	500
Pb	2.5	5	10	25	50	100	250	500
B	2.5	5	10	25	50	100	250	500
As	25	50	100	250	500	1000	2500	5000
Al	2.5	5	10	25	50	100	250	500
Zn	2.5	5	10	25	50	100	250	500

4. Analyze a complete set of spiked samples, including a blank, for certification.
5. Analyze a set of three spiked samples (2x, 5x and 10x) and a blank with each lot for quality control.

5. PROCEDURE

A. SAMPLE PREPARATION

1. Weigh 1.0-gram soil samples and quantitatively transfer to 100-mL beakers.

2. Add 3.0 mL of concentrated nitric acid; cover the beakers with watch glasses, place on a hot plate, evaporate to near dryness, and cool.
3. Repeat Step 2 until the digestion is complete.
4. Add 2.0 mL of 1+1 HNO₃ and 2.0 mL of 1+1 HCl to the residue, and heat until the residue dissolves.
5. Wash down the sides of the beakers and the watch glass covers with deionized water.
6. Filter the samples through nitric-acid-washed Gelman 42-mm glass-fiber filter pads.
7. Dilute each sample to a final volume of 50.0 mL with deionized water.

B. CALIBRATION AND ANALYSIS

Perform the procedures for simultaneous analysis described in the manufacturer's operator's manual.

6. CALCULATIONS

- A. The spectrometer provides direct readout of solution concentrations.
- B. Determine the concentration of metal in soil/sediment matrix (on a dry-weight basis) according to the following formula:

$$\text{Concentration (ug/g)} = \frac{\text{ug/L metal} \times V_e}{W_d}$$

where: W_d = dry weight of sample in extract (in grams)

V_e = volume of extract (in liters)

7. REFERENCES

Federal Register. Vol. 44, No 233, Monday, December 3, 1979.
Inductively Coupled Plasma (ICP) Optical Emission Spectrometric
Method for Trace Element Analysis of Water and Wastes.

8. DATA

SECTION G

ANALYSIS OF ARSENIC IN SOILS BY ATOMIC ABSORPTION,
FURNACE TECHNIQUE: USATHAMA CERTIFIED METHOD B9 FOR UBTL;
AND USATHAMA CERTIFIED METHOD G9 FOR CAL

DEVELOPED FROM
EPA METHOD 7060, SW-846, 2ND ED, JULY 1982

USATHAMA CERTIFIED METHOD B9 FOR UBTL

USATHAMA CERTIFIED METHOD
Analysis of Arsenic in Soils and Solids by
Graphite-Furnace Atomic Absorption Spectroscopy (GF-AA)

I. Application: This method is applicable to the quantitative determination of arsenic (As) in soils and solid samples.

- A. Tested Concentration Range: 2.5 µg/g to 50 µg/g. (The observed background level in standard soil is 3.6 µg/g).
- B. Sensitivity: 45 milliabsorbance units at detection limit of 2.5 µg/g.
- C. Detection Limit: 2.5 µg/g. (Certified range: 2.5 µg/g-50 µg/g)
- D. Interferences: Elemental arsenic and many of its compounds are volatile and therefore samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digests prior to analysis to minimize volatilization losses during drying and ashing.

In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (197.2 nm). Simultaneous background correction must be employed to avoid erroneously high results.

If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

- E. Analysis Rate: One analyst can prepare 20 samples in an eight hour day and analyze them during the following 8 hour day.

II. Chemistry

- A. Alternate Nomenclature and Chemical Abstracts Register Number: 7440-38-2

B. Physical/Chemical Properties:

atomic weight = 74.92
mp = 818°C (36 mm)
bp = N/A

C. Chemical Reactions: N/AIII. Apparatus

A. Instrumentation: Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer equipped with a Model HGA-500 graphite furnace/autosampler accessory. Pyrolytic-coated graphite tubes with L'vov platforms are used.

B. Parameters:

1. Wavelength: 197.2 nm (bandwidth 0.7 nm, low).
2. Lamp and Current: HCL, 18 ma.
3. Graphite Furnace: (See attached sheet for exact furnace settings).
 - a. Drying cycle, 55 sec. programmed from 90°C to 110°C
 - b. Ashing cycle, 30 sec. ramp from 110°C to 1200°C
 - c. Atomizing cycle, 5 sec. at 2500°C
4. Background Correction: Continuous deuterium arc.

C. Hardware/Glassware:

1. 125 mL Phillips beakers.
2. Watch glasses.
3. Thermometer (0° - 200°C).
4. 100 mL volumetric flasks, volumetric pipettes, (various volumes as required) and Eppendorf pipettes (various volumes as required).
5. Hot plate and water bath.

D. Chemicals:

1. Nitric acid, conc., Baker Instra-analyzed or equivalent.
2. Hydrogen peroxide, 30%, reagent grade.

3. ASTM Type II water (water must be monitored for As).
4. Arsenic SARM stock solution (1000 μg As per mL).
5. Nickel nitrate hexahydrate, reagent grade.

E. Reagents:

1. Nitric acid 1:1 (v:v), by dilution of D-1 above.
2. 0.1% Nickel modifier solution prepared by dissolving 0.4956 g of nickel nitrate hexahydrate in 100 mL of water.
3. Nitric acid 2% (v:v), by dilution of D-1 above.

IV. Standards

A. Working Standard Solution: Dilute 2.0 mL of conc. nitric acid and 1.00 mL of the 1000 $\mu\text{g}/\text{mL}$ arsenic stock solution with water in a 100 mL volumetric flask; this is the working standard (10 $\mu\text{g}/\text{mL}$).

B. Calibration Standards: From the working standard solution, prepare calibration standards by adding the indicated volumes to 100 mL volumetric flasks and diluting to volume with 2% nitric acid.

<u>Standard</u>	<u>Volume (mL) of 10 $\mu\text{g}/\text{mL}$ Arsenic Working Standard</u>	<u>Final Concentration of Arsenic Standard Solution</u>
A	0	0
B	0.25	0.025
C	0.50	0.050
D	1.00	0.100
E	1.50	0.150
F	2.00	0.200
G	2.50	0.250
H	3.00	0.300

Use 20 μL of each standard solution combined with 20 μL of modifier to generate a standard curve. The correlation coefficient of the linear regression fit must be 0.995 or greater.

C. Control and Certification Spikes: Prepare the following spiked samples using 1.0 g portions of standard soil and the working standard (10 $\mu\text{g}/\text{mL}$). Analyze these samples as described in Part V below. Note that most of the digests will require

dilution prior to GF/AA determination. Certification and control samples are allowed to stand for at least one hour after spiking before proceeding with the analysis.

<u>Designation</u>	<u>Volume (mL) of 10.0 (µg/mL) Standard Added</u>	<u>µg/g added to Soil</u>	<u>µg/mL in 100 mL Digest</u>
"Method Blank"	0.0	0.0	0.0
0.5x	0.25	2.5	0.025
1x	0.50	5.0	0.05
2x	1.0	10.0	0.10
5x	2.5	25	0.25
10x	5.0	50	0.50

(x = 5 µg/g)

Daily quality control requires the use of only the "Method Blank," two control spikes at the 25 µg/g level and one control spike at the 10 µg/g level.

V. Procedures:

- A. Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh and transfer to a 125 mL Phillips beaker a 1.0 g portion (to the nearest 0.01 g) of sample.
- B. Add 10 mL of 1:1 nitric acid, mix the slurry, and cover with a watch glass. Heat the sample to 95°C for 10 minutes without boiling. Allow the sample to cool, add 5 mL of conc. nitric acid, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.
- C. After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H₂O₂). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.
- D. Continue to add 30% H₂O₂ in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (Note: Do not add more than a total of 10 mL 30% H₂O₂.) Remove the watch glass and continue heating the acid-peroxide digest until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the

mixture. After cooling, filter through Whatman No. 42 filter paper and dilute to 100 mL with Type II water. The diluted digest solution contains approximately 2% (v:v) nitric acid.

- E. Autosampler cuvettes are filled with about 2 mL of the final digests. The autosampler is programmed to combine 20 μ L of sample digest and 20 μ L of modifier. Responses are compared to the linear standard curve. Analyze the 0.150 μ g/mL arsenic standard after every 10 samples. If this standard exceeds the \pm 10% continuing calibration check criteria (i.e., the result is outside the 0.135 to 0.165 μ g/mL range), then the AA must be recalibrated and the previous set of 10 samples must be rerun.

During routine analysis, a set of five calibration standards (A,B,D,F & H) are analyzed at the beginning of the run and at the end of the run. The two sets of calibration data are combined to make the calibration plot for the samples in the run. All samples are analyzed twice and the average of the two runs is reported as the result.

If any sample responses exceed that of the highest calibration standard (0.300 μ g/mL), aliquots of the digests are diluted with 2% nitric acid and reanalyzed.

VI. Calculations

$$\mu\text{g As/g soil sample} = \frac{(\mu\text{g/mL conc. found})(100 \text{ mL})(\text{dilution factor})}{(\text{g sample analyzed})}$$

The results are corrected for recovery and reported on a dry weight basis.

- VII. References: Method 3050 from SW-846, "Test Methods for Evaluating Solid Waste," USEPA, July 1982.

METHOD 3050

ACID DIGESTION OF SLUDGES

1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

Antimony	Lead
Arsenic	Nickel
Barium	Selenium
Beryllium	Silver
Cadmium	Thallium
Chromium	Zinc
Copper	

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Tl.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers.

4.2 Watch glasses.

2 / WORKUP TECHNIQUES - Inorganic

- 4.3 Drying ovens that can be maintained at 30° C.
- 4.4 Thermometer that covers range of 0° to 200° C.
- 4.5 Whatman No. 42 filter paper or equivalent.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Weigh and transfer to a 250-ml conical Phillips' beaker a 1.0-g portion of sample which has been dried at 60° C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample at 95° C and reflux for 10 min. Allow the sample to cool, add 5 ml of conc. HNO_3 , replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2 .)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3 . For analysis, withdraw aliquots of appropriate volume, add any required reagent or matrix modifier, and analyze by method of standard additions.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

CERTIFICATION RESULTS - ARSENIC - UBTL - 7/8/85
 RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	3.340	3.380	3.880	3.850
2.500	5.460	5.780	5.900	5.720
5.000	7.360	7.650	8.680	7.740
10.000	11.690	11.850	13.050	12.440
25.000	28.350	27.810	28.330	28.770
50.000	53.740	53.640	52.600	54.070

12.8 2.7 2.7 2.7 2.7

CERTIFICATION RESULTS - ARSENIC - UBTL - 7/8/85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 15.416666667 SD= 17.8408828663

FOUND CONC
MEAN= 18.545 SD= 17.9882280346

N0. RUNS 4 TOTAL X-Y ALL RUNS 24 N0. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 3.01015936255

SLOPE= 1.00766533865

USE FOR ACCURACY

R= 0.999411350612

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.398144549103

ST ERROR EST= 0.630986964289

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 22

TWO TAIL P LEVEL IS .1

t= 1.71713909197

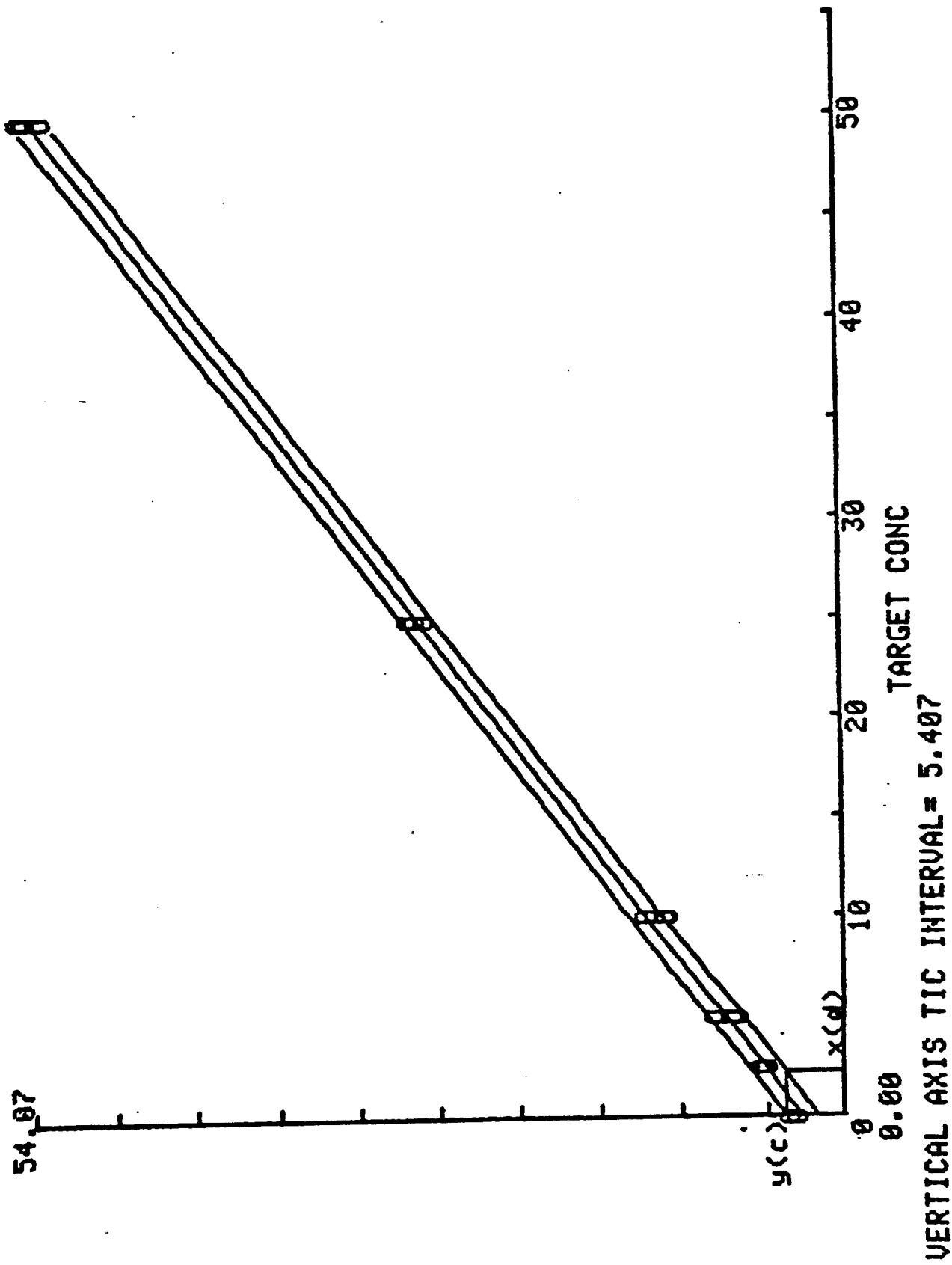
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

y(c)= 4.13309457074

x(d)= 2.22426786616

CERTIFICATION RESULTS - ARSENIC - UBTL - 7/8/85
RUNS 1 2 3 4
FOUND CONC



CERTIFICATION RESULTS - ARSENIC - UBTL - 7/8/85
 RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT
 INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	3.613	0.292		8.091
2.500	5.715	0.186	128.600	3.250
5.000	7.858	0.572	57.150	7.277
10.000	12.258	0.619	22.575	5.050
25.000	28.315	0.393	13.260	1.388
50.000	53.513	0.635	7.025	1.188
Means		0.450	45.722	4.374

USATHAMA CERTIFIED METHOD G9 FOR CAL

USATHAMA CERTIFIED METHOD #G9
Analysis of Arsenic in Soils and Solids by
Graphite-Furnace Atomic Absorption Spectroscopy (GF-AA)

(CAL Version 6 6/12/85)
(USATHAMA Version 1, 6/12/85)

I. Application: This method is applicable to the quantitative determination of arsenic (As) in soils and solid samples.

- A. Tested Concentration Range: 5.0 ug/g to 100 ug/g.
- B. Sensitivity: 0.02 abs. units at 0.010 ug/mL.
- C. Detection Limit: 5.0 ug/g. Accuracy: 0.985
- D. Interferences: None.
- E. Analysis Rate: One analyst can prepare and analyze 20 samples in an eight hour day.

II. Chemistry:

- A. Alternate Nomenclature and Chemical Abstracts Register Number: N/A
- B. Physical/Chemical Properties:
 - atomic weight = 74.92
 - mp = 818°C (36 mm)
 - bp = N/A
- C. Chemical Reactions: N/A

III. Apparatus:

- A. Instrumentation: Perkin-Elmer Model Zeeman/3030 Atomic Absorption Spectrophotometer (or equivalent) equipped with a Model HGA-600 graphite furnace (or equivalent). Pyrolytic-coated graphite tubes with graphite platforms are recommended.
- B. Parameters:
 - 1. Wavelength: 193.7 nm (bandwidth 0.7 nm).
 - 2. Lamp and Current: EDL, 8 watts.

3. Graphite Furnace:
 - a. Drying cycle, 30 sec. at 125°C.
 - b. Ashing cycle, 30 sec. at 1200°C.
 - c. Atomizing cycle, 3 sec. at 2300°C.

C. Hardware/Glassware:

1. 250 mL Teflon beakers.
2. Watch glasses.
3. Thermometer (0° - 200°C).
4. Volumetric flasks, volumetric pipettes, and Eppendorff pipettes.
5. Hot plate and water bath or sand bath.

D. Chemicals:

1. Nitric acid, conc., Baker Instra-analyzed or equivalent.
2. Hydrogen peroxide, 30%.
3. ASTM Type II water (water must be monitored for As).
4. Arsenic SARM stock solution (1000 ppm).
5. Nickel nitrate hexahydrate, reagent grade.

E. Reagents:

1. 1:1 (v:v) Nitric acid, by dilution of D-1 above.
2. 0.02% Nickel modifier solution prepared by dissolving 0.0991 g of nickel nitrate hexahydrate in 100 mL of water.
3. 2% (v:v) Nitric acid, by dilution of D-1 above.

IV. Standards:

- A. Standard Solutions: Dilute 2.0 mL of conc. nitric acid and 1.0 mL of the 1000 ug/mL arsenic stock solution with water in a 100 mL volumetric flask; this is the spiking standard (10 ug/mL). Dilute 2.0 mL of conc. nitric acid and 0.60 mL of spiking standard with water in a 100 mL volumetric flask; this is the working (calibration) standard (0.060 ug/mL).
- B. Calibration Standards: The autosampler modifier solution reservoir, dilution water reservoir, and working standard solution reservoir are filled with 0.02% nickel nitrate, 2% nitric acid, and 0.060 ug/mL arsenic, respectively. The autosampler is programmed to generate a standard curve from the following combinations:

Volume (uL) of 0.060 ug/mL As	Volume (uL) 2% HNO ₃	Volume (uL) Ni(NO ₃) ₂ mod.	Final As conc. (ug/mL)
0.0	9.0	20	0.0
3.0	6.0	20	0.020
6.0	3.0	20	0.040
9.0	0.0	20	0.060

The standard curve is acceptable (linear) if the correlation coefficient is 0.995 or greater.

- C. Control and Certification Spikes: Prepare the following spike samples using 1.0 g portions of standard soil and the spiking standard (10 ug/mL). Analyze these samples as described in part V below. Note that most of the digests will require dilution prior to GF/AA determination.

Designation	Volume of 10.0 (ug/mL) standard added	ug/g added to soil	ug/mL in 100 mL digest
"Method Blank"	0.0	0.0	0.0
0.5x	0.50	5.0	0.05
1x	1.0	10	0.10
2x	2.0	20	0.20
5x	5.0	50	0.50
10x	10.0	100	1.0

Note that the standard soil contains an apparent background level of 2.0 ug/g of arsenic.

Daily quality assurance requires the analysis of unspiked standard soil (the "Method Blank"), a spike at 10 ug/g, and duplicate spikes at 25 ug/g with each batch of samples. These daily spikes are prepared by adding 1.0 mL and 2.5 mL of the 10.0 ug/mL standard to 1.0 g of standard soil, allowing the spikes to set for one hour, and then proceeding as in V below.

V. Procedures:

- A. Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh and transfer to a teflon beaker a 1.0 g portion (to the nearest 0.01 g) of sample.
- B. Add 10 mL of 1:1 nitric acid mix the slurry and cover with a watch glass. Heat the sample to 95°C for 10 minutes without boiling. Allow the sample to cool, add 5 mL of conc. nitric acid, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.
- C. After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.
- D. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (Note: Do not add more than a total of 10 mL 30% H_2O_2 .) Continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper and dilute to 100 mL with Type II water. The diluted digestate solution contains approximately 2% (v:v) nitric acid.
- E. Autosampler cuvettes are filled with about 1.5 mL of the final digestates. The autosampler is programmed to combine 9.0 uL of sample digestate and 15 uL of modifier (as in the calibration step, IV-B). Responses are compared to the standard curve. Analyze the 0.040 ug/mL arsenic standard after every

10 samples. If this standard exceeds the $\pm 10\%$ continuing calibration check criteria (i.e., the result is outside the 0.044 to 0.036 ug/mL window), then the AA must be recalibrated and the previous set of 10 samples must be rerun.

If any sample responses exceed that of the highest calibration standard (0.060 ug/mL), then dilute the digests with 2% nitric acid and reanalyze.

VI. Calculations:

$$\text{ug As/g soil sample} = \frac{(\text{ug/mL conc. found})(\text{mL final Vol.})}{(\text{g sample analyzed})}$$

The results are corrected to a dry weight basis.

VII. References: Modification of Method 3050 from SW-846
"Test Methods for Evaluating Solid Waste",
USEPA, July 1982.

METHOD 3050

ACID DIGESTION OF SLUDGES

1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

Antimony	Lead
Arsenic	Nickel
Barium	Selenium
Beryllium	Silver
Cadmium	Thallium
Chromium	Zinc
Copper	

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Tl.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers.

4.2 Watch glasses.

2 / WORKUP TECHNIQUES - Inorganic

- 4.3 Drying ovens that can be maintained at 30° C.
- 4.4 Thermometer that covers range of 0° to 200° C.
- 4.5 Whatman No. 42 filter paper or equivalent.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Weigh and transfer to a 250-ml conical Phillips' beaker a 1.0-g portion of sample which has been dried at 60° C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample at 95° C and reflux for 10 min. Allow the sample to cool, add 5 ml of conc. HNO_3 , replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2 .)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3 . For analysis, withdraw aliquots of appropriate volume, add any required reagent or matrix modifier, and analyze by method of standard additions.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

RECEIVED

MAY 02 1985

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	1.900	2.000	2.100	1.800
5.000	6.200	6.500	6.700	6.100
10.000	9.900	9.900	11.000	11.000
20.000	19.000	22.000	20.000	22.000
50.000	50.000	52.000	51.000	55.000
100.000	98.000	100.000	100.000	100.000

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

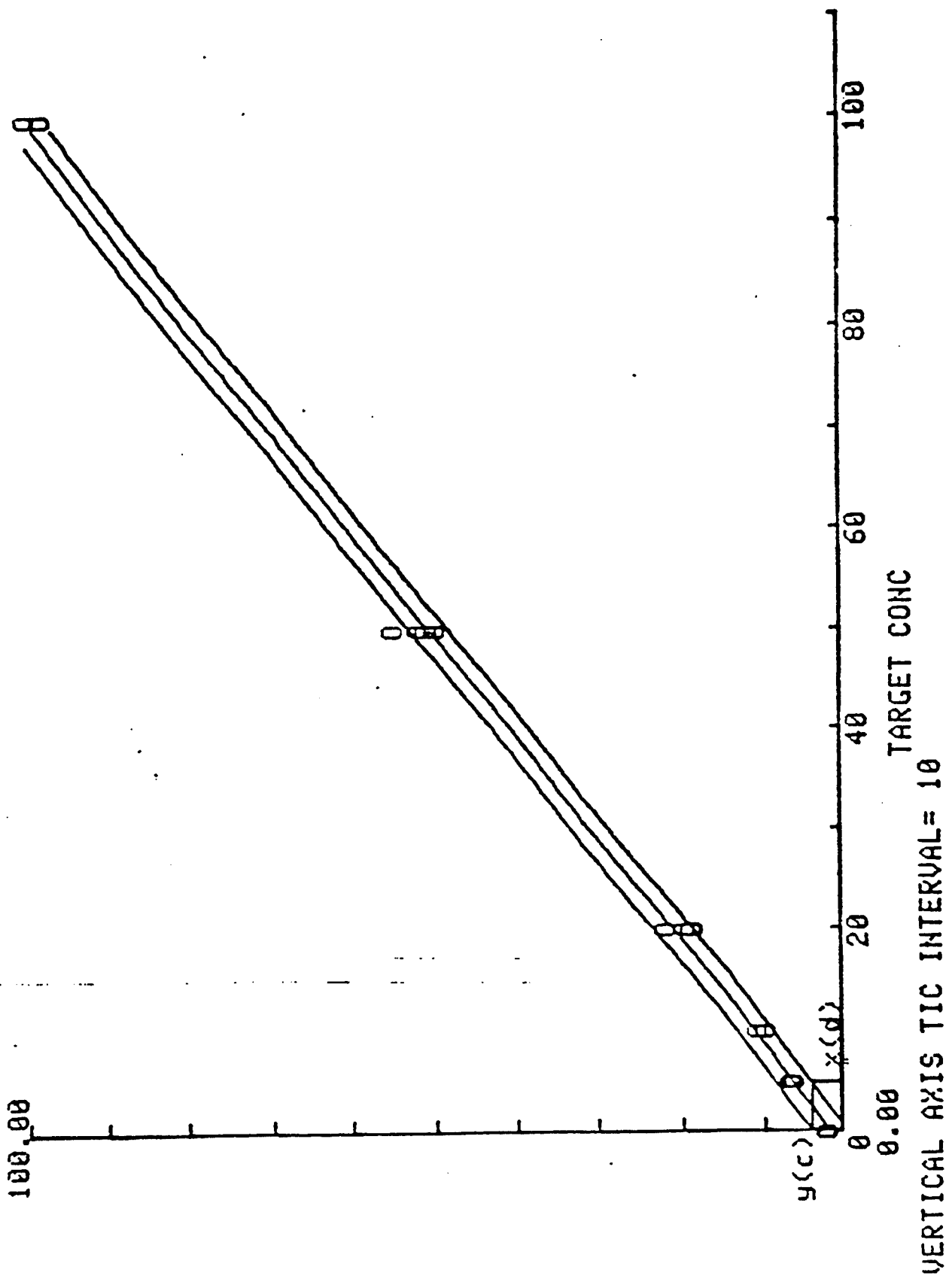
TARGET CONC
MEAN= 30.833333333 SD= 35.6817657326

FOUND CONC
MEAN= 31.8375 SD= 35.1716512883

NO. RUNS 4 TOTAL X-Y ALL RUNS 24 NO. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 1.46491178145
SLOPE= 0.985056915196
USE FOR ACCURACY
R= 0.999343755378
MEAN SQR DEV OF POINTS FROM REGRESSION= 1.6968517489
ST ERROR EST= 1.30263262238
USE FOR PRECISION
T FOR CONFIDENCE BAND
D.F.= 22
TWO TAIL P LEVEL IS .1
t= 1.71713909197
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE
MEASURED 1 TIME(S))
y(c)= 3.7831403944
x(d)= 4.69675994515

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85
RUNS 1 2 3 4
FOUND CONC



CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85

RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT

INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	1.950	0.129		6.620
5.000	6.375	0.275	27.500	4.320
10.000	10.450	0.635	4.500	6.077
20.000	20.750	1.500	3.750	7.229
50.000	52.000	2.160	4.000	4.154
100.000	99.500	1.000	-0.500	1.005
Means		0.950	7.850	4.901

RECEIVED

MAY 04 1985

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC.

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	1.900	2.000	2.100	1.800
5.000	6.200	6.500	6.700	6.100
10.000	9.900	9.900	11.000	11.000
20.000	19.000	22.000	20.000	22.000

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 4 TARGET CONC-MEAN FOUND CONCENTRATION (REPORT) POINTS

TARGET CONC
MEAN= 8.75 SD= 8.5391256383

MEAN FOUND CONCENTRATION (REPORT)
MEAN= 9.88125 SD= 8.03433711744

NO. RUNS 4 TOTAL X-Y ALL RUNS 16 NO. CONCENTR 4
MEASURES (Y'S) EACH TARGET CONC 4

INTERCEPT= 1.66
SLOPE= 0.939571428571
USE FOR ACCURACY
R= 0.998603662935
MEAN SQR DEV OF POINTS FROM REGRESSION= 0.270214285721
ST ERROR EST= 0.519821397906

USE FOR PRECISION
T FOR CONFIDENCE BAND

D.F.= 2

TWO TAIL P LEVEL IS .1

t= 2.91998064954

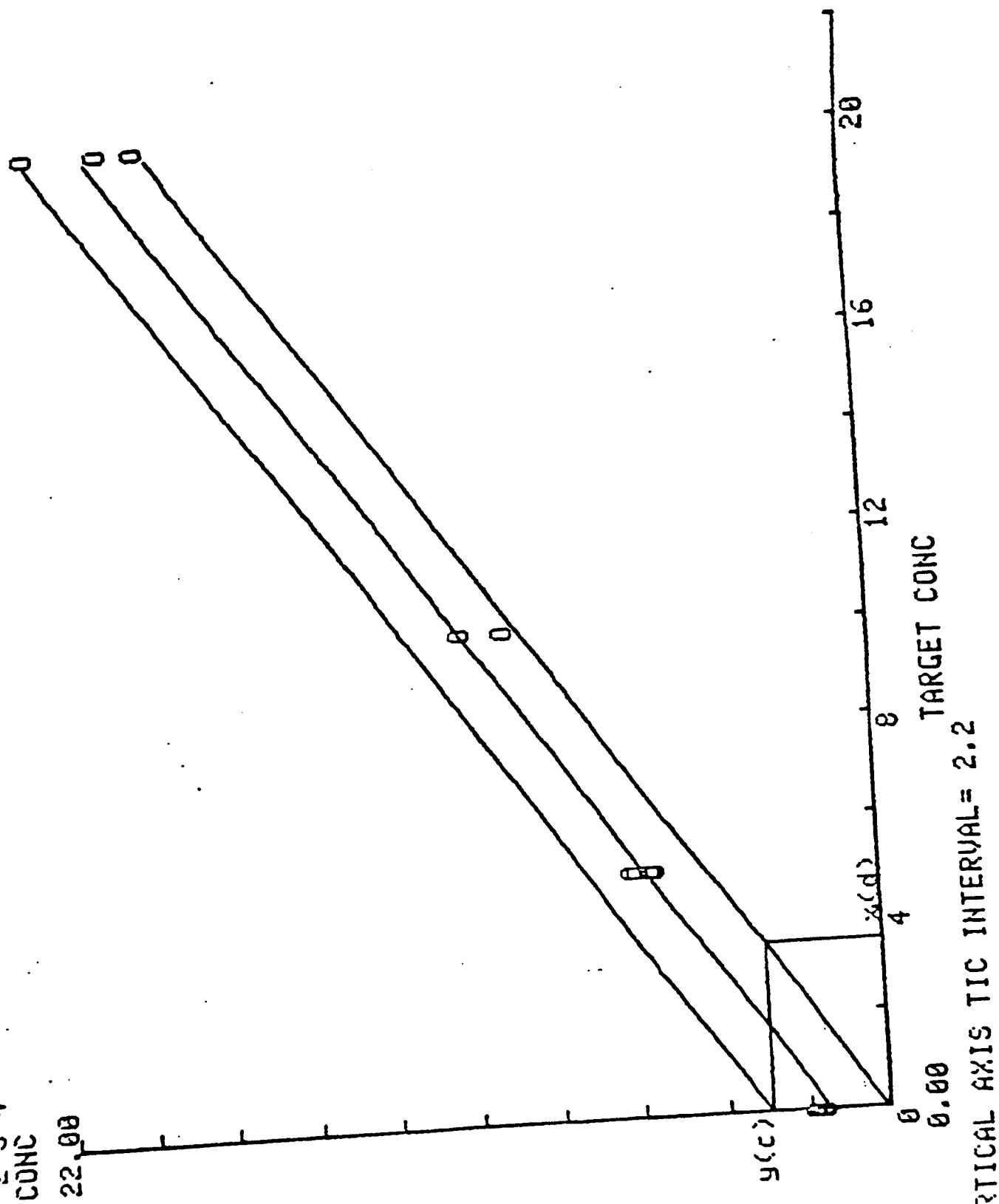
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 4 TIME(S))

y(c)= 3.05940554071

x(d)= 2.80398473422

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85
 RUNS 1 2 3 4
 FOUND CONC



RTICAL AXIS TIC INTERVAL= 2.2

CERTIFICATION RESULTS - CAL LAB - ARSENIC - 5-1-85
 RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT
 INACCURACY AND IMPRECISION

Mn Targt Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	1.950	0.129		6.620
5.000	6.375	0.275	27.500	4.320
10.000	10.450	0.635	4.500	6.077
20.000	20.750	1.500	3.750	7.229
Means		0.635	11.917	6.062

SECTION H

ANALYSIS OF MERCURY IN SOILS BY COLD VAPOR
ATOMIC ABSORPTION SPECTROSCOPY (CVAAS):
USATHAMA CERTIFIED METHOD Y9 FOR UBTL; AND
USATHAMA CERTIFIED METHOD J9 FOR CAL

DEVELOPED FROM
EPA METHOD 245.5, EPA-600/4-79-020 REVISED MARCH 1983

USATHAMA CERTIFIED METHOD Y9 FOR UBTL

ANALYSIS OF MERCURY IN SOILS BY COLD VAPOR
ATOMIC ABSORPTION SPECTROSCOPY (CVAAS)

- I. Application : This method is applicable for the quantitative determination of mercury (Hg) in soils or solid samples.
- A. Tested Concentration Range - 0.05 $\mu\text{g/g}$ to 1.00 $\mu\text{g/g}$.
 - B. Sensitivity - Peak height in mm at detection limit: 19 mm at 0.05 $\mu\text{g/g}$.
 - C. Detection Limit - ($\mu\text{g/g}$ in soil sample) - 0.05 $\mu\text{g/g}$
 - D. Interferences - Possible interference from sulfide is eliminated by the addition of aqua regia and potassium permanganate.
 - E. Analysis Rate - One analyst can prepare 20 samples in an 8 hour day. One analyst can analyze 20 samples in an 8 hour day.
- II. Chemistry
- A. Alternate Nomenclature and Chemical Abstracts Register Number - N/A.
 - B. Physical and Chemical Properties - Mercury, Hg M.W. = 200.59; Melting Pt. - 39°C ; Boiling Pt. 357°C .
 - C. Chemical Reactions - N/A.
- III. Apparatus
- A. Instrumentation - Atomic absorption spectrophotometer- Perkin-Elmer Model 305-B equipped with Hg hollow cathode lamp, cold vapor accessory, and strip chart recorder.

B. Parameters

1. Wavelength: 253.7 nm.
2. Purge gas flow (air): 1 Liter/min.
3. Hollow cathode lamp current: 6 ma.
4. Sample aliquot: 50 mL.

C. Hardware/Glassware

1. BOD Bottles, 300-mL.
2. Watch glasses, 50-mm.
3. Volumetric flasks, 10 mL, 250-mL, 1000-mL.
4. Volumetric pipets (glass or Eppendorf type)
5. Steam bath.
6. Pipet bulb.
7. Phillips beakers, 250 mL.

D. Chemicals

1. Hydrochloric acid, conc., reagent grade.
2. Nitric acid, conc., Baker Instra-analyzed, or equivalent.
3. Hydroxylamine hydrochloride, reagent grade.
4. Stannous chloride dihydrate, reagent grade.
5. Potassium permanganate, reagent grade.
6. Mercury solution: SARM supplied by USATHAMA which was 500 mL of 0.1% w/v mercury in dilute nitric acid from MCB. The actual lot analysis certified by USATHAMA was 1008 ppm.

E. Reagents

1. Aqua Regia: Prepare before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3 .
2. Stannous chloride 10%: To 100 g stannous chloride dihydrate, add 500 mL conc. HCl. Stir until dissolved. Dilute to 1000 mL with distilled water.
3. Hydroxylamine hydrochloride solution: Dissolve 200 g of hydroxylamine hydrochloride in distilled water and dilute to 1 liter.

4. Potassium permanganate - 5% solution, w/v: Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

IV. Standards

A. Calibration Standards

1. Add approximately 5 mL of distilled water and .5 mL of concentrated HNO_3 to a 10 mL volumetric flask. To this flask add 1.0 mL of the 1000 $\mu\text{g/mL}$ mercury stock solution and dilute to volume, giving a solution of 100.0 $\mu\text{g/mL}$ Hg. This solution may be stored up to one week. To a second 10 mL volumetric flask, add 5 mL distilled water, 0.5 mL concentrated HNO_3 and 0.1 mL of the 100.0 $\mu\text{g/mL}$ mercury solution. Dilute to volume, giving a solution of 1.0 $\mu\text{g/mL}$ Hg. This solution must be prepared fresh daily. Transfer 0, 0.04, 0.10, 0.25, 0.50, 0.75 and 1.25 mL aliquots of the 1.0 $\mu\text{g/mL}$ mercury solution to a series of 250 mL Phillips beakers and immediately cover with a watch glass. The amounts are summarized below.

<u>Volume (mL)</u> <u>of 1.0 $\mu\text{g/mL}$</u> <u>Standard Added</u>	<u>Total Hg (μg)</u> <u>per 250 mL</u>	<u>Hg (μg) per</u> <u>50 mL Aliquot</u>
0	0	0.000
.04	0.04	0.008
.10	0.10	0.020
.25	0.25	0.050
.50	0.50	0.100
.75	0.75	0.150
1.25	1.25	0.250

Follow the sample preparation and analysis procedure given in Section V starting with the addition of aqua regia. Construct a standard curve by plotting instrument response versus micrograms of mercury as described in Section VI.

B. Control Spikes

1. For certification weigh one gram portions of the standard soil into each of six 250-mL Phillips beakers. Record the exact soil weight. To the beaker, add the following amounts of the 1.0 $\mu\text{g/mL}$ Hg standard prepared in IV. A.

<u>Designation</u>	<u>Amount (mL) of 1.0 $\mu\text{g/mL}$ Standard Added</u>	<u>Total Hg (μg) per 250 mL</u>	<u>μg Hg/50 mL Aliquot</u>
Blank	0.00	0	0.00
0.5X	0.05	0.05	0.01
X	0.10	0.10	0.02
2X	0.20	0.20	0.04
5X	0.50	0.50	0.10
10X	1.00	1.00	0.20

After addition of the mercury standard the control spikes are allowed to stand for one hour. The control spikes are then treated as samples following the procedure given in Section V.

2. Daily quality control requires the use of only the method blank (unspiked standard soil), the X level spike (0.10 $\mu\text{g/g}$), and duplicate 5X level spikes (0.50 $\mu\text{g/g}$). For daily quality control weigh one gram portions of the standard soil into each of four 250-mL Phillips beakers. Record the exact soil weight. To the beaker, add the following amounts of 1.0 $\mu\text{g/mL}$ Hg standard prepared in IV.A.

<u>Designation</u>	<u>Amount (mL) of 1.0 $\mu\text{g/mL}$ Standard Added</u>	<u>Total Hg (μg) per 250 mL</u>	<u>μg Hg/50 mL Aliquot</u>
Blank	0.00	0	0.00
X	0.10	0.10	0.02
5X	0.50	0.50	0.10
5X	0.50	0.50	0.10

After addition of the mercury standard the control spikes are allowed to stand for one hour. The control spikes are then treated as samples following the procedure given in Section V.

V. Procedure

Weigh one gram portions of the soil samples. Record the exact soil weight and place in separate 250-mL Phillips beakers. The Phillips beakers should be covered with watch glasses during heating. To each beaker, add 25 mL of aqua regia. Heat 5 minutes on a steam bath. Cool and add 50 mL distilled water and 25 mL potassium permanganate solution to each sample. Mix thoroughly and return to the steam bath. If a solution does not remain purple for at least 10 minutes, add an additional 5 mL of potassium permanganate solution and return it to the steam bath. Repeat until purple color remains at least 10 minutes. Cool, transfer to a 250-mL volumetric flask, dilute to volume with distilled water, and mix thoroughly. Transfer an aliquot of the solution (normally 50-mL) into each of two BOD bottles. Add 50 mL of distilled water (or whatever volume is required to bring the volume of liquid in the BOD bottles up to 100 mL). Add 5 mL of 20% hydroxylamine hydrochloride solution to reduce the excess permanganate. Expel the air in the head space of the BOD bottle by passing clean air into it. Add 5 mL of the stannous chloride solution and immediately insert the bubbler, which closes the aeration system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has been previously adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, open the system by removing the bubbler. Rinse the bubbler with distilled water and dry. When the recorder trace levels off at its minimum value, another sample can be analyzed.

An aliquot of each calibration standard is analyzed at the beginning of the run. Duplicate aliquots of samples are then analyzed, interspersed with aliquots of mid-range standards at intervals of ten samples. The run is concluded with the analysis of a second aliquot of each of the calibration standards. It should be noted that the "zero level" calibration standard as described in Section IV.A.1 is the reagent blank.

Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation.

- VI. Calculations - Prepare a standard curve for the micrograms of mercury present in the standards versus peak heights. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Calculate the mercury concentration in the sample by the formula:

$$\mu\text{g Hg/g soil sample} = \frac{\mu\text{g Hg in the aliquot} \times 250 \text{ mL}}{(\text{vol. of aliquot in mL}) \times (\text{wt of soil sample in g})}$$

The results are corrected for recovery based upon the certification data and for moisture content and then reported on a dry weight basis.

- VII. References - Method 245.5 (Mercury in Sediment) In: "Methods for chemical Analysis of Water and Wastes. EPA 600/4-79-020, U.S. Environmental Protection Agency: Cincinnati, Ohio, March 1979. The method has been scaled up to allow for reanalysis of smaller aliquots of highly concentrated samples.

MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
 - 1.1 This procedure⁽¹⁾ measures total mercury (organic + inorganic) in soils, sediments, bottom deposits and sludge type materials.
 - 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
 - 2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
 - 2.2 An alternate digestion⁽²⁾ involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
 - 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
 - 3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
 - 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
 - 4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the head air space in the BOD bottle should be purged before the addition of stannous sulfate.
5. Apparatus
 - 5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.
- NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.
- NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.
6. Reagents
- 6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO₃.
- 6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.
- NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.
- 6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.
- 6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 µg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the

working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of KMnO_4 solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass value and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass value, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 N KMnO_4 and 10% H_2SO_4
- b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a BOD bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated KMnO_4 solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-

hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu\text{g Hg/g} = \frac{\mu\text{g Hg in the aliquot}}{\text{wt of the aliquot in gms}}$$

9.3 Report mercury concentrations as follows: Below 0.1 $\mu\text{g/g}$, <0.1; between 0.1 and 1 $\mu\text{g/g}$, to the nearest 0.01 μg ; between 1 and 10 $\mu\text{g/g}$, to nearest 0.1 μg ; above 10 $\mu\text{g/g}$, to nearest μg .

10. Precision and Accuracy

10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 $\mu\text{g/g} \pm 0.02$ and 0.82 $\mu\text{g/g} \pm 0.03$. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
2. Salma, M., private communication, EPA Cal/Nev Basin Office, Alameda, California.

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.026	0.012	0.005	0.009
0.050	0.085	0.048	0.058	0.056
0.100	0.119	0.080	0.106	0.091
0.200	0.210	0.230	0.215	0.199

Use For detection limit only
ML
 5/2/85

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 16 TARGET CONC-FOUND CONC POINTS

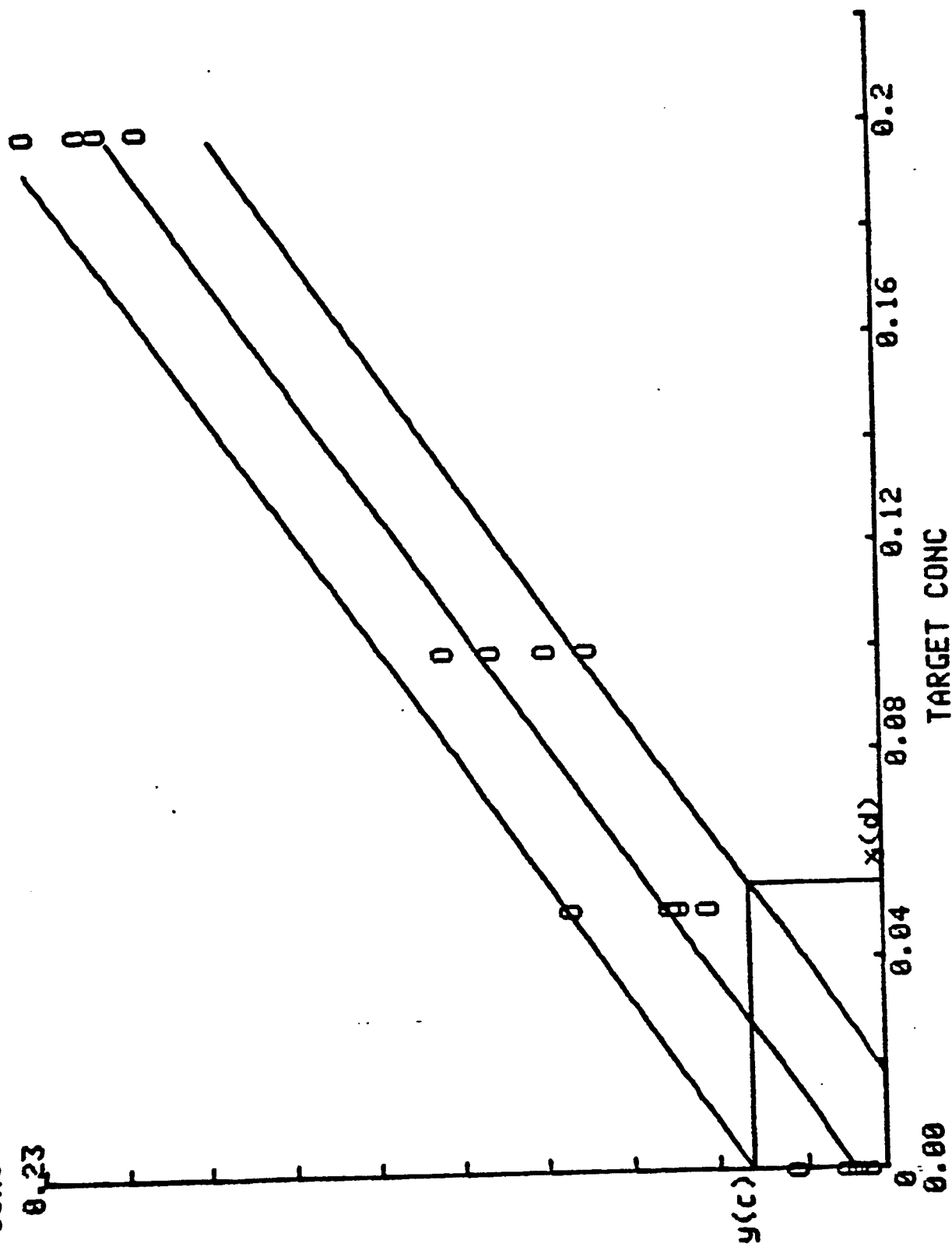
TARGET CONC
MEAN= 0.0875 SD= 0.0763762615826

FOUND CONC
MEAN= 0.0968125 SD= 0.077415087892

NO. RUNS 4 TOTAL X-Y ALL RUNS 16 NO. CONCENTR 16
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 0.0096
SLOPE= 0.996714285714
USE FOR ACCURACY
R= 0.983339463684
MEAN SQR DEV OF POINTS FROM REGRESSION= 2.121780612E-4
ST ERROR EST= 0.0145663331427
USE FOR PRECISION
T FOR CONFIDENCE BAND
D.F.= 14
TWO TAIL P LEVEL IS .1
t= 1.7613101065
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE
MEASURED 1 TIME(S))
y(c)= 0.0371128123224
x(d)= 0.0542930802906

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85
 RUNS 1 2 3 4
 FOUND CONC



TARGET CONC

VERTICAL AXIS TIC INTERVAL= 0.023

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85
 RUNS 1 2 3 4
 STATISTICAL DATA USED TO DETERMINE PERCENT
 INACCURACY AND IMPRECISION

Nn Target Con UG/G	Nn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.013	0.009		70.221
0.050	0.062	0.016	23.500	26.058
0.100	0.099	0.017	-1.000	17.241
0.200	0.214	0.013	6.750	6.029
Means		0.014	9.750	29.887

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85
 RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.026	0.012	0.005	0.009
0.050	0.085	0.048	0.058	0.056
0.100	0.119	0.080	0.106	0.091
0.200	0.210	0.230	0.215	0.199
0.500	0.546	0.548	0.530	0.512
1.000	1.055	1.100	1.110	1.059

Use for accuracy & precision only.
 Wth 5/2/85

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.308333333333 SD= 0.356817657326

FOUND CONC
MEAN= 0.333708333333 SD= 0.383647197437

N0. RUNS 4 TOTAL X-Y ALL RUNS 24 N0. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 0.00252902675014
SLOPE= 1.07409504838

USE FOR ACCURACY

R= 0.998990525514

MEAN SQR DEV OF POINTS FROM REGRESSION= 3.135841763E-4

ST ERROR EST= 0.0177083081148

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 22

TWO TAIL P LEVEL IS .1

t= 1.71713909197

X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C

(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

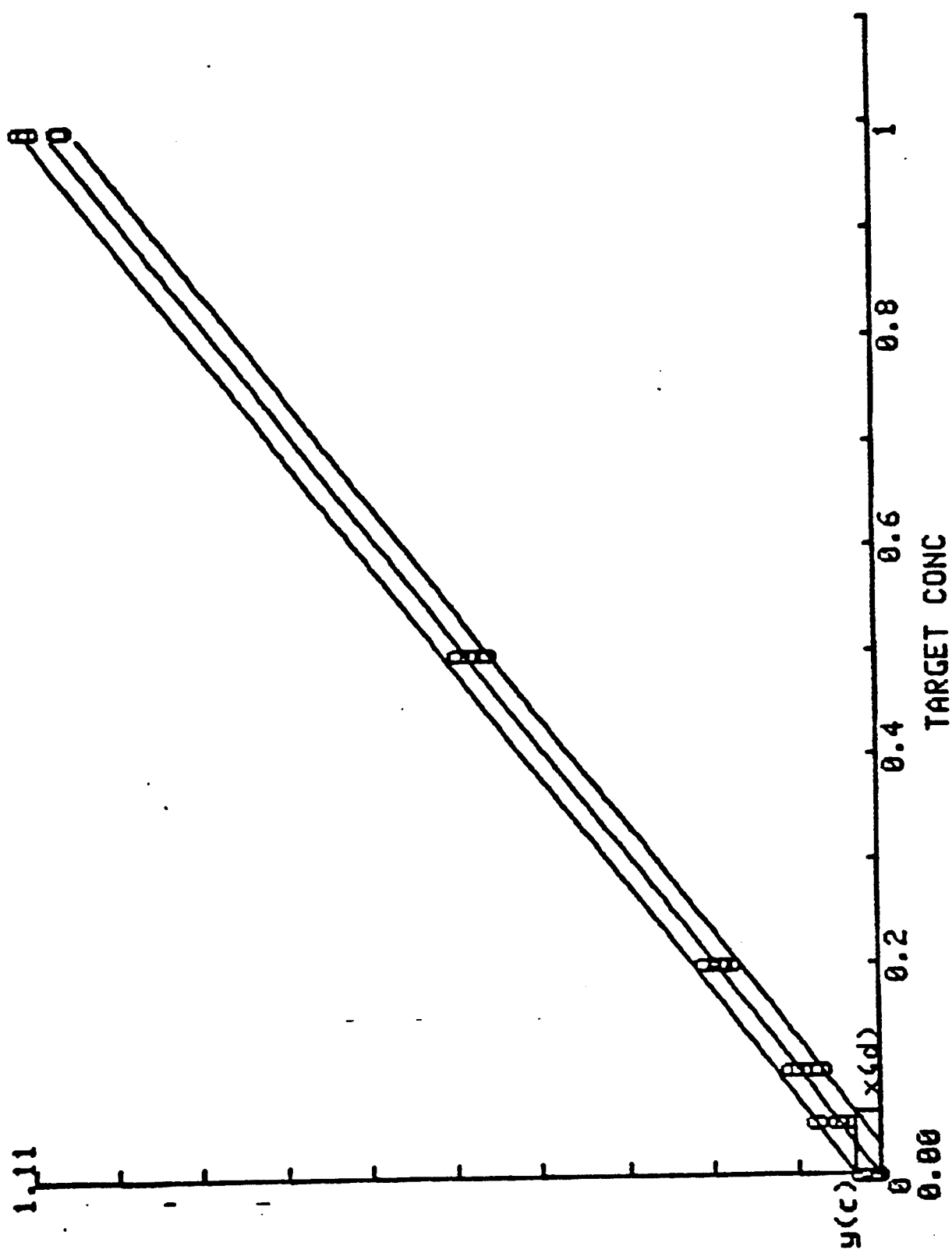
y(c)= 0.0340435964401

x(d)= 0.0585284001653

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85

RUNS 1 2 3 4

FOUND CONC



VERTICAL AXIS TIC INTERVAL= 0.111

CERTIFICATION RESULTS - UBTL - MERCURY - 5-1-85

RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT

INACCURACY AND IMPRECISION

Mn Target Conc UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.013	0.009		70.221
0.050	0.062	0.016	23.500	26.058
0.100	0.099	0.017	-1.000	17.241
0.200	0.214	0.013	6.750	6.029
0.500	0.534	0.017	6.800	3.134
1.000	1.081	0.028	8.100	2.596
Means		0.017	8.830	20.880

USATHAMA CERTIFIED METHOD J9 FOR CAL

USATHAMA CERTIFIED METHOD #J9
Determination of Mercury in Soils by Cold Vapor
Atomic Absorption Spectroscopy (CVAAS)

(CAL Version 5, 6/1/85)
(USATHAMA Version 2, 6/1/85)

- I. Application: This method is applicable for the quantitative determination of mercury (Hg) in soils or solid samples.
- A. Tested Concentration Range:
0.05 ug/g to 1.0 ug/g
- B. Sensitivity: Peak height at 0.1 ug/g is 14 mm.
- C. Detection Limit: 0.06 ug/g Accuracy: 1.014
- D. Interferences: Possible interference from sulfide is eliminated by the addition of aqua regia and potassium permanganate. Possible interference from chlorine is eliminated by purging the BOD bottle head space prior to addition of stannous chloride.
- E. Analysis Rate: One analyst can prepare and analyze 20 samples in an eight hour day.
- II. Chemistry:
- A. Alternate Nomenclature and Chemical Abstracts Register Number: N/A.
- B. Physical and Chemical Properties: M.W. = 200.59;
Melting Pt. - 39°C; Boiling Pt. 357°C.
- C. Chemical Reactions: N/A.
- III. Apparatus:
- A. Instrumentation: Fisher Mercury Analyzer equipped with Hg hollow cathode lamp, cold vapor accessory, and strip chart recorder.

B. Parameters:

1. Wavelength: 253.7 nm.
2. Purge gas flow (air): about 2 Liter/min.
3. Hollow cathode lamp current: 6 ma.
4. Sample aliquot: 50 mL.

C. Hardware/Glassware:

1. BOD Bottles, 300 mL.
2. Watch glasses, 50 mm.
3. Volumetric flasks, 100 mL, 250 mL, 1000 mL.
4. Volumetric pipets (glass or Eppendorf type).
5. Steam bath.
6. Pipet bulb.
7. Teflon beakers, 250 mL.
8. Plastic funnels.

D. Chemicals:

1. Hydrochloric acid, conc., Baker ULTREX grade, or equivalent.
2. Nitric acid, conc., Baker ULTREX grade, or equivalent.
3. Hydroxylamine hydrochloride, reagent grade.
4. Stannous chloride dihydrate, reagent grade.
5. Potassium permanganate, reagent grade.
6. Mercury solution: SARM supplied by USATHAMA which was 500 mL of 0.1% w/v mercury in dilute nitric acid from MCB. The actual lot analysis certified by USATHAMA was 1008 ppm.
7. Magnesium perchlorate, reagent grade (to be used as a drying agent).

E. Reagents:

1. Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to volume of conc. HNO₃.
2. Stannous chloride 10%: To 100 g stannous chloride dihydrate, add 500 mL conc. HCl. Stir until dissolved. Dilute to 1000 mL with distilled water.
3. Hydroxylamine hydrochloride solution 20%: Dissolve 200 g of hydroxylamine hydrochloride in distilled water and dilute to 1 liter.
4. Potassium permanganate 5%: Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

F. Glassware Cleaning Protocol:

1. Due to the low detection limit of the method, the ubiquitous nature of mercury, and the use of aqua regia for digestions, all glassware must be scrupulously cleaned as follows prior to use:
2. Teflon beakers must be rinsed with dilute hydroxylamine hydrochloride to eliminate adsorbed KMnO₄.
3. All glassware must be decontaminated after use as follows:
 - a. Discard digestates, digested soils, etc. as appropriate and immediately rinse with water.
 - b. Wash with detergent and rinse with DI water.
 - c. Soak for 10 min. in warm 1:1 nitric acid (prepared daily), rinse twice with DI water followed by two rinses with distilled water. Goggles or safety glasses, gloves and acid-resistant apron are mandatory!
 - d. Allow containers to dry on a clean surface in an inverted position. Store in a dust-free area.
4. Remove the mercury apparatus absorbance cell after each run and clean as described above.

IV. Standards:

A. Calibration Standards:

1. Add approximately 50 mL of distilled water and 5.0 mL of concentrated HNO_3 to a 100 mL volumetric flask. To this flask add 1.0 mL of the 1000 ug/mL mercury stock solution and dilute to volume, giving a solution of 10.0 ug/mL Hg. This intermediate solution may be stored up to one week.
2. To a second 100 mL volumetric flask, add 50 mL distilled water, 5.0 mL concentrated HNO_3 and 10 mL of the 10.0 ug/mL mercury solution. Dilute to volume, giving a working solution of 1.0 ug/mL Hg. This solution must be prepared fresh daily.
3. Transfer 0, 0.04, 0.10, 0.25, 0.50, 0.75 and 1.25 mL aliquots of the 1.0 ug/mL working solution to a series of 250 mL Teflon beakers and immediately cover with a watch glass. The amounts are summarized on Page 4.

<u>Volume (mL) of 1.0 ug/mL working Standard Added</u>	<u>Total Hg (ug) per 250 mL</u>	<u>Hg (ug) per 50 mL Aliquot</u>
0	0	0.000
.04	0.04	0.008
.10	0.10	0.020
.25	0.25	0.050
.50	0.50	0.100
.75	0.75	0.150
1.25	1.25	0.250

Follow the sample preparation and analysis procedure given in Section V starting with the addition of aqua regia. Construct a standard curve by plotting instrument response versus micrograms of mercury as described in Section VI.

B. Control Spikes:

1. For certification weigh one gram portions of the standard soil into each of six 250 mL Teflon beakers. Record the exact soil weight. To the beaker, add the following amounts of the 1.0 ug/mL working standard.

<u>Designation</u>	<u>Amount (mL) of 1.0 ug/mL working Standard Added</u>	<u>Total Hg (ug) per 250 mL</u>	<u>Hg (ug) per 50 mL Aliquot</u>
Blank	0.00	0	0.00
0.5X	0.05	0.05	0.01
X	0.10	0.10	0.02
2X	0.20	0.20	0.04
5X	0.50	0.50	0.10
10X	1.0	1.0	0.20

After addition of the mercury standard the control spikes are allowed to stand for one hour. The control spikes are then treated as samples following the procedure given in Section V.

- Daily quality assurance requires the analysis of unspiked standard soil (the "Method Blank"), a spike at 0.10 ug/g, and duplicate spikes at 0.50 ug/g with each batch of samples. These daily spikes are prepared by adding the spike standards indicated below to 1.0 g of standard soil, allowing the spikes to sit for one hour, and then proceeding as in V below.

<u>Designation</u>	<u>Amount (mL) of 1.0 ug/mL Standard Added</u>	<u>Total Hg (ug) per 250 mL</u>	<u>Hg (ug) per 50 mL Aliquot</u>
Blank	0.00	0	0.00
2X	0.10	0.10	0.02
5X	0.50	0.50	0.10
5Xdup	0.50	0.50	0.10

After addition of the mercury standard the control spikes are allowed to stand for one hour. The control spikes are then treated as samples following the procedure give in Section V.

V. Procedure:

Weight 1.0 gram portions of the soil samples. Record the exact soil weight and place in separate 250 mL Teflon beakers. The Teflon beakers should be covered with watch glasses during heating. To each beaker, add 25 mL of aqua regia. Heat 5 minutes on a steam bath. Cool and add 50 mL distilled water and 25 mL potassium

permanganate solution to each sample. Mix thoroughly and return to the steam bath. If a solution does not remain purple for at least 10 minutes, add an additional 5 mL of potassium permanganate solution and return it to the steam bath. Repeat until purple color remains at least 10 minutes. Cool, transfer to a 250 mL volumetric flask, dilute to volume with distilled water, and mix thoroughly. Transfer an aliquot of solution (normally 50 mL) into each of two BOD bottles. Add 50 mL of distilled water (or whatever volume is required to bring the volume of liquid in the BOD bottles up to 100 mL). Add 5 mL of 20% hydroxylamine hydrochloride solution to reduce the excess permanganate. Using a separate purge system, expel the air in the head space of the BOD bottle by passing clean air into it. Add 5 mL of the stannous chloride solution and immediately insert the bubbler, which closes the aeration system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has been previously adjusted to a rate of 2 liter per minute, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 seconds. As soon as the recorder pen levels off, open the system by removing the bubbler. Rinse the bubbler with distilled water and dry. When the recorder trace levels off at its minimum value, another sample can be analyzed.

The Fisher Mercury Analyzer should be operated as follows:

1. Turn power on and allow a ten minute warm-up period. Make sure knobs A and B on the back of the analyzer are in the full counter-clockwise position and the AGC button is off. The auto-zero switch should be on "Manual" and the scalar switch set a 1X (middle position). The zero knob and gain knob are at mid position.
2. Turn knob B on the back of the analyzer in a clockwise direction and line the needle on the absorbance meter up with the 100% reading. Readjust the setting to 100% absorbance until the needle stabilizes at this setting for at least 15 minutes.
3. Turn knob A on the back of the analyzer in a clockwise direction and line the needle on the absorbance meter up with the zero percent absorbance reading. Readjust the setting to zero percent absorbance until the needle stabilizes at this setting for at least 15 minutes.

4. Switch the scalar control to 10X absorbance. Adjust zero knob to zero percent absorbance reading.
5. Turn on air flow through analyzer cell.
6. Readjust zero control until the absorbance stabilizes at zero for at least 15 minutes.
7. Begin analysis as described in Section V.
8. The magnesium perchlorate should be changed after approximately 30 analyses.

An aliquot of each calibration standard is analyzed at the beginning of the run. Duplicate aliquots of samples are then analyzed, interspersed with aliquots of mid-range standards at intervals of ten samples. The run is concluded with the analysis of a second aliquot of each of the calibration standards. It should be noted that the "zero level" calibration standard as described in Section IV. A. 1. is the reagent blank.

Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Always conduct the analysis in a hood. Empty the used BOD bottles into a waste container in the hood.

- VI. Calculations: Prepare a standard curve for the micrograms of mercury present in the standards versus peak heights. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g soil sample} = \frac{\text{ug Hg in the aliquot} \times 250 \text{ mL}}{(\text{vol. of aliquot in mL}) \times (\text{wt of soil sample in g})}$$

The results are then reported on a dry weight basis.

- VII. References: Method 245.5 (Mercury in Sediment) In: "Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020, U.S. Environmental Protection Agency: Cincinnati, Ohio, March 1979. The method has been scaled up to allow for reanalysis of smaller aliquots of highly concentrated samples. A copy is attached.

MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
 - 1.1 This procedure¹ measures total mercury (organic + inorganic) in soils, sediments, bottom deposits and sludge type materials.
 - 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
 - 2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
 - 2.2 An alternate digestion¹ involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
 - 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
 - 3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
 - 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
 - 4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the BOD bottle should be purged before the addition of stannous sulfate.
5. Apparatus
 - 5.1 Atomic Absorption Spectrophotometer (See Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3) The apparatus is assembled as shown in the accompanying diagram.
- NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO₃.
- 6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.
- NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.
- 6.6 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg
- 6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 µg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the

working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of KMnO_4 solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 N KMnO_4 and 10% H_2SO_4
- b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219, Cat. # 580-13 or # 580-22.

8. Procedure

- 8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a BOD bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).
- 8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated KMnO_4 solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-

hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation

9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu\text{g Hg/g} = \frac{\mu\text{g Hg in the aliquot}}{\text{wt of the aliquot in gms}}$$

9.3 Report mercury concentrations as follows: Below 0.1 $\mu\text{g/gm}$, <0.1; between 0.1 and 1 $\mu\text{g/gm}$, to the nearest 0.01 μg ; between 1 and 10 $\mu\text{g/gm}$, to nearest 0.1 μg ; above 10 $\mu\text{g/gm}$, to nearest μg .

10. Precision and Accuracy

10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 $\mu\text{g/g} \pm 0.02$ and 0.82 $\mu\text{g/g} \pm 0.03$. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
2. Salma, M., private communication, EPA Cal/Neu Basin Office, Alameda, California.

RECEIVED

MAY 02 1985

CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.050	0.060	0.058	0.070	0.054
0.100	0.110	0.120	0.130	0.130
0.200	0.220	0.170	0.210	0.230
0.500	0.490	0.430	0.580	0.530
1.000	1.100	0.950	1.100	0.950

CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 24 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.30833333333 SD= 0.356817657326

FOUND CONC
MEAN= 0.3205 SD= 0.36423797763

N0. RUNS 4 TOTAL X-Y ALL RUNS 24 N0. CONCENTR 24
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 0.00773733636881

SLOPE= 1.01436539556

USE FOR ACCURACY

R= 0.993700564867

MEAN SQR DEV OF POINTS FROM REGRESSION= 0.00174195586486

ST ERROR EST= 0.0417367447803

USE FOR PRECISION

T FOR CONFIDENCE BAND

D.F.= 22

TWO TAIL P LEVEL IS .1

t= 1.71713909197

X(C) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C

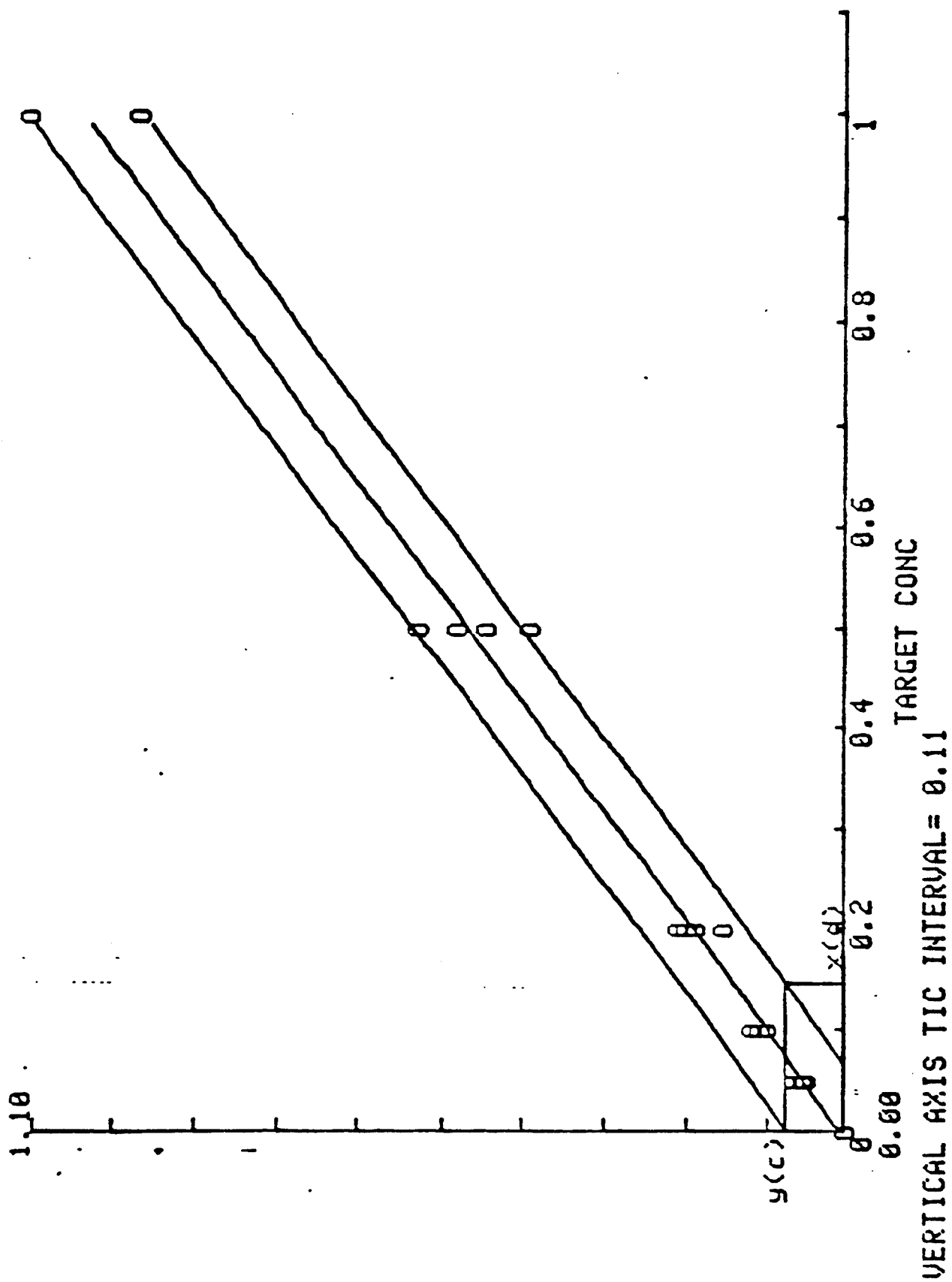
(EACH TARGET CONC CONSIDERED INDEP SAMPLE

MEASURED 1 TIME(S))

y(c)= 0.0020140850842

x(d)= 0.145646770872

CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85
 RUNS 1 2 3 4
 FOUND CONC



CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85

RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT INACCURACY AND IMPRECISION

Mn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.050	0.061	0.007	21.000	11.251
0.100	0.123	0.010	22.500	7.816
0.200	0.208	0.026	3.750	12.674
0.500	0.508	0.063	1.500	12.501
1.000	1.025	0.087	2.500	8.449
Means		0.032	10.250	10.538

MAY 04 1985

CERTIFICATION RESULTS - CAL LAD - MERCURY - 5-1-85

RUNS 1 2 3 4

COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/G	Day 1 Found Conc UG/G	Day 2 Found Conc UG/G	Day 3 Found Conc UG/G	Day 4 Found Conc UG/G
0.000	0.000	0.000	0.000	0.000
0.050	0.060	0.058	0.070	0.054
0.100	0.110	0.120	0.130	0.130
0.200	0.220	0.170	0.210	0.230

CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85
RUNS 1 2 3 4
ANALYSIS OF 16 TARGET CONC-FOUND CONC POINTS

TARGET CONC
MEAN= 0.0875 SD= 0.0763762615826

FOUND CONC
MEAN= 0.097625 SD= 0.0803698741237

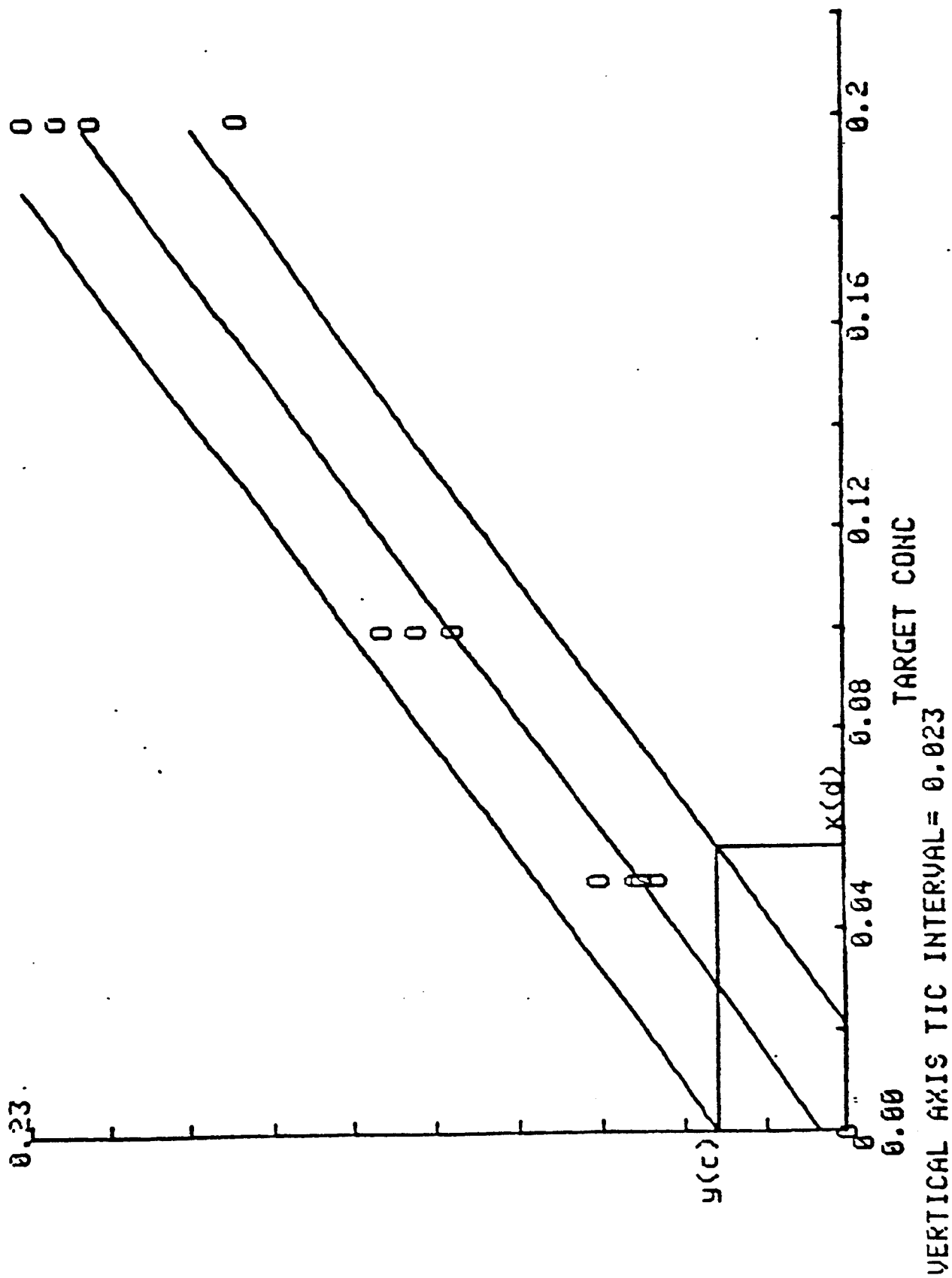
N0. RUNS 4 TOTAL X-Y ALL RUNS 16 N0. CONCENTR 16
MEASURES (Y'S) EACH TARGET CONC 1

INTERCEPT= 0.0072
SLOPE= 1.03342857143
USE FOR ACCURACY
R= 0.98207707501
MEAN SQR DEV OF POINTS FROM REGRESSION= 2.45855102E-4
ST ERROR EST= 0.0156797672827
USE FOR PRECISION
T FOR CONFIDENCE BAND
D.F.= 14
TWO TAIL P LEVEL IS .1
t= 1.7613101065
X(D) FOR CALIBRATION CURVE OR UNKNOWN SAMPLE? C/U C
(EACH TARGET CONC CONSIDERED INDEP SAMPLE
MEASURED 1 TIME(S))
Y(C)= 0.0368158607854
X(d)= 0.0563474083827

CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85
RUNS 1 2 3 4
FOUND CONC

RUNS 1 2 3 4

FOUND COND



CERTIFICATION RESULTS - CAL LAB - MERCURY - 5-1-85
 RUNS 1 2 3 4

STATISTICAL DATA USED TO DETERMINE PERCENT
 INACCURACY AND IMPRECISION

Nn Target Con UG/G	Mn Found Conc UG/G	Standard Deviation	Mean Pct Inaccuracy	Imprecision
0.000	0.000	0.000		
0.050	0.061	0.007	21.000	11.251
0.100	0.123	0.010	22.500	7.816
0.200	0.208	0.026	3.750	12.674
Means		0.011	15.750	10.580

SECTION I

ORGANIC MATERIAL IN SOILS

DEVELOPED BY UBTL, JANUARY 1985

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680

Dissolved 00681

1. Scope and Application

- 1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
- 1.2 The method is most applicable to measurement of organic carbon above 1 mg/l.

2. Summary of Method

- 2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

3. Definitions

- 3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
 - A) soluble, nonvolatile organic carbon; for instance, natural sugars.
 - B) soluble, volatile organic carbon; for instance, mercaptans.
 - C) insoluble, partially volatile carbon; for instance, oils.
 - D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
 - E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
- 3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

Approved for NPDES

Issued 1971

Editorial revision 1974

4. **Sample Handling and Preservation**

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($\text{pH} \leq 2$) with HCl or H_2SO_4 .

5. **Interferences**

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. **Apparatus**

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. **Reagents**

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

- 7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

- 7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

- 8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

- 8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

- 9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574-79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).